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The alkaline hydrolysis of some ortho-substituted ethyl benzoates

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THE ALKALINE HYDROLYSIS OF

SOME ORTHO-SUBSTITUTED ETHYL BENZOATES

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CONTENTS

A B S T R A C T

Rate constants for the saponification of four ortho substituted benzoic esters have been measured over a range of temperatures in 60% (w/v) dioxan-water, using a spectrophotometric technique for following the rate of reaction. The results for one compound, ethyl o-toluate, have been checked by a titration technique.

Thermodynamic activation parameters have been calculated for the esters studied, and their values have been discussed in terms of substituent and solvent effects.

The ultraviolet spectra of five other esters have been measured in the solvent indicated. The spectrophotometric technique has been found to be unsuitable for the study of rates of saponification of these esters, and the applicability and facility of this technique have been discussed.

Difficulties have been encountered due to the reaction of hydroxyl ion with a solvent impurity, 2-methyl-1, 3-dioxolane, but aqueous dioxan has been found to be a suitable solvent for the study of ester hydrolysis reactions if it has been carefully purified.

A I M S

In the Taft method of analysing substituent effects into polar and steric components the range of ortho substituents for which substituent parameters σ^* and E_s are available is limited to the following nine substituents: OCH_3, OEt, F, Cl, Br, I, CH_3, NO_2, C_6H_5. From many points of view it would be desirable to increase this range and this project is intended to be an exploratory study of the feasibility of measuring Taft parameters for new substituents in terms of the original ester hydrolysis definition.

The evaluation of a Taft σ^* parameter for a given substituent requires a determination of the rates of both acidic and basic hydrolysis of the ester containing that substituent. The majority of previous studies of acid catalysed ester hydrolyses have been made in aqueous acetone solutions while aqueous alcohols have been the most favoured solvents for alkaline studies of this reaction. As a result a large number of Taft σ^* values have been derived from measurements in which the acidic and basic hydrolyses were carried out in different solvents. With the increasing awareness of the importance of solvation factors in substituent effects it is clearly desirable that all measurements required for σ^* values (as well as E_s values) should be made in a single solvent. Neither of the two solvents mentioned (aqueous acetone and aqueous alcohol) is really suitable for studies under both acidic and basic

conditions and one purpose of this investigation is to examine the possibility of using aqueous dioxan as a general solvent for such studies. Some previous workers had reported difficulties with this solvent.

Since the commencement of this work (1967), considerable doubt has been thrown on the relevance of the Taft analysis to ortho substituent effects by the work of Charton. This has given a particular topicality to these studies.

A further aim of this work is to investigate the adequacy of a spectrophotometric technique for the study of the hydrolysis of ortho substituted benzoic esters.

I N T R O D U C T I O N

(a) KINETIC AND THERMODYNAMIC RELATIONSHIPS

(i) Derivation of Kinetic Equations

A bimolecular reaction of the form

$$A + B \longrightarrow \text{products},$$

whose rate is first order with respect to the concentration of each component can have its rate represented [1,2] by

$$\frac{dx}{dt} = k_2(a-x)(b-x),$$

where a and b are the initial concentrations of components A and B respectively, x is the concentration of A or B reacted at time t, and k_2 is the second order specific rate constant.

If initially a = b,

$$\frac{dx}{dt} = k(a-x)^2.$$

When integrated between the limits $x = 0 \longrightarrow x$ and $t = 0 \longrightarrow t$,

$$\frac{x}{a(a-x)} = kt. \qquad \ldots\ldots \qquad (1)$$

If reactant B is present in large excess (relative to A), the reaction displays pseudo first order kinetic form with respect to the concentration of reactant A, and the rate equation can be represented by

$$\frac{dx}{dt} = k_1(a-x), \qquad \ldots\ldots \qquad (2)$$

where k_1 is the pseudo first order rate constant, and

$$k_1 = k_2 b, \qquad \ldots\ldots \qquad (3)$$

b being assumed to be constant during the reaction, i.e. $b-x \doteqdot b$.

When equation (2) is integrated between the limits $x = 0 \longrightarrow x$ and $t = 0 \longrightarrow t$,

$$\ln \frac{a}{a-x} = k_1 t. \qquad \ldots\ldots \qquad (4)$$

If the concentration is measured spectrophotometrically, from the Beer-Lambert law (see page 22), providing the wavelength of the incident radiation is constant,

$$\frac{a}{a-x} = \frac{A_o - A_\infty}{A_t - A_\infty}, \qquad \ldots\ldots \qquad (5)$$

where A_o, A_t and A_∞ are the absorbances initially, at time t, and at infinite time respectively.

Equation (4) becomes

$$\ln \frac{A_o - A_\infty}{A_t - A_\infty} = k_1 t, \qquad \ldots\ldots \qquad (6)$$

which can be written

$$c - \ln(A_t - A_\infty) = k_1 t, \qquad \ldots\ldots \qquad (7)$$

where c is a constant.

(ii) Reaction Rate Theories

The first attempt to relate the velocity of a chemical change to reaction temperature was made by S.A. Arrhenius [3,4] in 1889 in a study of the acid catalysed inversion of cane sugar.

He proposed that

$$k = Ae^{-E_a/RT}, \qquad \ldots\ldots \quad (8)$$

where k is the specific reaction rate constant, A and E_a are empirical constants, R is the molar gas constant and T is the absolute temperature.

The term $e^{-E_a/RT}$ is the expression derived from the Boltzmann distribution for the fraction of a molecular system having energy in excess of E_a [5]. Arrhenius interpreted E_a as the energy threshold required to make a molecule "active", i.e. able to react, and this energy term has become known as the "energy of activation".

The pre-exponential term A has the same units as k, and is often referred to as the "frequency factor", although it only possesses frequency units for a first order reaction.

The Arrhenius equation is the most frequently used method of quantifying the temperature dependence of rates of reactions and similar physical processes [6-9]. Equation (8)

may be re-written as

$$\log k = \frac{-E_a}{2.303R}\left(\frac{1}{T}\right) + \log A,$$

from which it is clear that plots of log k against $(1/T)$ should be linear (and values of E_a and A may be obtained from such plots) providing both E_a and A are independent of temperature.*

The mechanical interpretation of the factor A is not clear. Attempts were made in bimolecular reactions to equate A with the collision number Z [10], which is given by the kinetic theory equation

$$Z = \sigma^2_{A,B}\left[8\pi k_B T\left(\frac{m_A + m_B}{m_A m_B}\right)\right]^{\frac{1}{2}},$$

where $\sigma_{A,B}$ is the mean collision diameter of molecules A and B, k_B is the Boltzmann constant (gas constant per molecule), and m_A and m_B are the masses of the molecular species A and B.

This gives a relationship of the form

$$k = BT^{1/2}e^{-E/RT} \qquad \ldots\ldots \quad (9)$$

and implies that the Arrhenius A factor is not constant with temperature, but is proportional to $T^{1/2}$.

Some reactions between simple ions in solution

* Ironically, the data for the inversion of sucrose on which Arrhenius based his theory exhibit a significant variation in E_a with temperature (11).

were found to be in quantitative agreement [12] with equation (9), i.e. A = Z, but many reactions were found to be much slower than predicted by the collision theory, and for these reactions a probability factor P was introduced into the equation,

$$k = PZe^{-E/RT}.$$

Values for P ranged as low as 10^{-8}, and various hypotheses which evolved to explain these low factors were never generally regarded as adequate [13].

Another weakness of the collision theory [14] is that for a reversible reaction it postulates that

$$K = \frac{k_1}{k_2} = e^{\frac{-(E_1 - E_2)}{RT}},$$

$$= e^{-\Delta H/RT} \qquad \ldots\ldots \quad (10)$$

where K is the equilibrium constant, the subscripts 1 and 2 refer to the forward and reverse reactions respectively, and the collision numbers Z_1 and Z_2 disappear because they are equal.

The expression (10) can only be true if the reaction involves no entropy change, i.e. ΔH is independent of temperature.

The Theory of Absolute Rates [15,16] postulates a "transition complex" which is in equilibrium with the reactants, and calculates reaction rate as the rate at which this complex decomposes to form products.

The reaction rate is calculated by applying statistical mechanics to the theoretical potential energy barrier which the transition complex must cross in the vibrational mode which will produce products.

From this theory is derived the relationship

$$k = \kappa \frac{k_B T}{h} K^* \qquad \ldots\ldots \quad (11)$$

where k is the specific reaction rate constant, k_B is the Boltzmann constant, K^* is the equilibrium constant for the equilibrium between the reactants and the transition complex, and κ is a transmission coefficient to allow for the probability that not every complex reaching the top of the potential barrier decomposes to form products.

The expression (11) gives a relationship of the form

$$k = B'Te^{-E/RT},$$

and implies that the Arrhenius A factor is proportional to T (cf. equation (19)).

The transmission coefficient κ is significantly less than unity for only two classes of gas phase reactions [17], but for reactions involving a simple ion in solution, e.g. OH^-, κ may be taken as unity [18].

The equilibrium constant K^* in equation (11) may be expressed in terms of free energy change by the familiar thermodynamic equation

$$\Delta G^* = -RT\ln K^*$$

where ΔG^* is the standard free energy change for the formation of the transition complex from the reactants.

Taking $K = 1$, equation (11) becomes

$$k = \frac{k_B T}{h} e^{\frac{-\Delta G^*}{RT}} . \qquad \ldots\ldots \quad (13)$$

If ΔG^* is replaced by its equivalent

$$\Delta G^* = \Delta H^* - T\Delta S^* \qquad \ldots\ldots \quad (14)$$

equation (13) may be written as

$$k = \frac{k_B T}{h} e^{\Delta S^*/R} e^{-\Delta H^*/RT} \qquad \ldots\ldots \quad (15)$$

where ΔH^* is the standard enthalpy of activation for the reactants to form the transition state, and ΔS^* is the standard entropy change for the formation of the transition state.

It can be shown [19] that, for reactions in solution, Arrhenius' energy of activation

$$E_a = \Delta H^* + RT, \qquad \ldots\ldots \quad (16)$$

and since at normal temperatures for reactions in solution RT is small, ($\div$ 600 cal mole^{-1}), the term ΔH^* in equation (16) can be regarded as approximately equal to E_a.

Comparison with equation (16) indicates that the Arrhenius equation (Equation (8)) is not able to take into account the entropy of activation, which for ester saponification reactions is a significant term, and it does not allow

for the variation of the pre-exponential term with temperature. Equation (15) has been preferred to equation (8) in assessing the rate-temperature relations in this project.

(b) MECHANISMS OF ESTERIFICATION AND SAPONIFICATION REACTIONS

(i) Esterification

The generally accepted mechanism [20] of esterification involves the reaction of an alcohol molecule with the carbonyl oxygen atom of the acid, followed by the elimination of a water molecule.

$$R - \overset{\overset{O}{\|}}{C} - OH + R'OH \rightleftharpoons R - \overset{\overset{O}{\|}}{C} - O - R' + H_2O$$

Disregarding steric factors, the rate of the reaction is dependent on the electron attracting powers of the carbonyl carbon atom, and this can be increased by the presence of an acid catalyst. The reaction is initiated by the attack of a hydrogen ion on the carbonyl oxygen atom. This provides a charged substrate (I) which is more readily attacked by the alcohol molecule.

$$R - \overset{\overset{O}{\|}}{C} - OH + H^+ \rightleftharpoons R - \overset{\overset{OH}{|}}{\underset{\underset{\oplus}{|}}{C}} - OH + R'OH$$

I

$$\rightleftharpoons \begin{matrix} R - C - OH \\ R - \overset{\oplus}{O}H \end{matrix} \rightleftharpoons R - \overset{\overset{O}{\|}}{C} - OR' + H_3O^+$$

II

The complex II forms the ester by elimination of a water molecule and a proton.

(ii) Saponification

Saponification of esters is frequently referred to as base catalysed, but, because hydroxyl ion is consumed in the reaction, Bender [21] points out that it should be more rigorously termed "nucleophilic-promoted hydrolysis".

Benzoic esters are known [22,23] to react by what Day and Ingold [24] term the $B_{AC}2$ mechanism, referring to a base catalysed bimolecular reaction involving fission of the acyl-oxygen bond.

$$R-\overset{\overset{O}{\|}}{C}-OR' + OH^- \overset{\text{slow}}{\rightleftharpoons} R-\overset{\overset{O^{\ominus}}{|}}{\underset{\underset{OH}{|}}{C}}-OR'$$

I

$$\xrightarrow{\text{fast}} R-\overset{\overset{O}{\|}}{C}-O^- + R'OH$$

The hydroxyl ion attacks the carbonyl carbon atom to form the SP^3 transition complex I. The complex then decomposes to form the acid anion and alcohol in an irreversible reaction. One notable feature of the saponification reaction is that in contrast to the esterification reaction it goes to completion. Bender [25] has provided evidence for the existence of a tetrahedral intermediate similar in structure to the SP^3 transition complex I by studies of

carbonyl oxygen exchange between esters and solvents.

(c) FREE ENERGY OF ACTIVATION

As indicated in equation (13), it is the free energy of activation (ΔG^*) which governs the rate of a chemical reaction at constant temperature [26,27], and factors which vary ΔG^* affect the rate of a reaction.

For the purposes of this project consideration of the factors affecting the rates of alkaline hydrolysis of ortho-substituted benzoic acids will be limited to substituent effects and solvent effects.*

It is common to resolve free energy of activation thermodynamically into enthalpy of activation and entropy of activation by equation (14)

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad \ldots\ldots \quad (14)$$

and substituent and solvent effects on ΔH^* and ΔS^* are discussed later under the headings Enthalpy of Activation and Entropy of Activation.

(i) The Linear Free Energy Principle

One approach to the effect of structure on reactivity involves the study of Linear Free Energy relationships. Hammett [30] noted that a large number of substituted

* It is assumed here that all the esters in a series react by the same mechanism. This assumption may not be valid in specific cases (28,29).

benzene side-chain reaction series obeyed a relationship of the form

$$\log \frac{k}{k_o} = \rho \log \frac{K}{K_o} \qquad \ldots\ldots \quad (17)$$

where k and k_o are the reaction rate constants of the substituted and unsubstituted compounds respectively, K and K_o are some other reaction constants for the substituted compounds (e.g. acid ionisation constants), and ρ is a constant specific to the particular reaction series considered.

Equation (17) implies that the free energy change

$$\delta\Delta G^* = \log k - \log k_o$$

produced by a substituent in one type of reaction is proportional to the free energy change produced by introduction of the same substituent in another type of reaction.

Hammett chose as his reference reaction series the ionisation constants of benzoic acids in water at 25°C., and defined

$$\sigma = \log \frac{K}{K_o}$$

as the substituent contribution to the free energy of activation of a substituted compound so that

$$\log \frac{k}{k_o} = \rho\sigma \qquad \ldots\ldots \quad (18)$$

By their mode of definition, Hammett's sigma values are positive for electron withdrawing substituents

(which increase the degree of dissociation of benzoic acids), and negative for electron releasing substituents. The value of the rho constant is specific to a particular reaction series, and for the ionisation of substituted benzoic acids has a value of +1.00. At the most elementary level, if the rate of a reaction is more sensitive to an electron withdrawing substituent than is the dissociation of its corresponding benzoic acid, ρ will have a value greater than +1.00, and vice versa. When comparing ρ values for two reaction series measured at different temperatures, however, this simple interpretation of the magnitude of ρ must be applied with caution (see part (d)).

Jaffe [31] tested the Hammett equation on 371 reaction series, and found it to correlate these data to an acceptable level of significance for approximately 90% of the series studied. Jaffe also noted that very many reaction series which obeyed the Hammett equation, contained one or two substituents having a significant deviation from the relationship.

The Hammett equation fails for reaction series in which steric effects influence the reaction rate [32,33], and saponification reactions of ortho substituted benzoic esters are one series which do not obey the Hammett equation.

(ii) The Ortho Effect

Taft [34] considered ortho substituent free

energy effects to be composed of independent contributions due to polar, resonance, and steric effects of the substituent.

Following on a suggestion of Ingold [35], he represented the polar effect of an ortho substituent as

$$\sigma^* = \frac{1}{2.48} \left(\log\left(\frac{k}{k_o}\right)_B - \log\left(\frac{k}{k_o}\right)_A\right),$$

where the subscripts B and A represent basic and acidic ester hydrolysis. Taft reasoned that steric and resonance effects are constant for hydrolysis in both media, and the observed change in free energy between these series can be attributed solely to the polar effect of the substituent. The factor 2.48 represents an arbitary constant chosen to give some correspondence between Taft's and Hammett's substituent constants.

For a reaction series in which resonance effects are not significant, he then assumed

$$\log \frac{k}{k_o} = \rho^*\sigma^* + E_s ,$$

where E_s is the steric contribution to free energy change.

He then reasoned from Hammett ρ values of meta and para substituted benzoates that acid catalysed hydrolyses of esters are influenced by polar effects to a neglible extent, i.e. $\rho^* \doteqdot 0$. From this assumption, E_s can be calculated as

$$E_s = \log \left(\frac{k}{k_o}\right)_A$$

for a substituent which does not conjugate with the benzene ring.

Values of σ^* are calculated relative to hydrogen as the standard substituent, i.e. ethyl benzoate is the reference compound. But ethyl benzoate exhibits resonance between the benzene ring and the carbonyl group, and for this reason is not used as a reference compound for the calculation of E_s values. In ethyl o-toluate the presence of the ortho substituent hinders this resonance by forcing the carboxyl group out of the plane of the ring [36], and values of E_s are calculated relative to the methyl group.

The Taft analysis produces results that are in good agreement with other data, such as electronegativities, dipole moments and van der Waal's radii. Its application to ortho substituents has, however, been subjected to recent severe criticism by Charton [37].

Table 1 lists some Taft values for σ^*, E_s, and, for purposes of comparison, Hammett substituent constants for para substituents (σ_p). A negative value for E_s indicates that the substituent exerts a larger steric effect than the methyl group.

TABLE 1

Substituent Constants [38-40]

Substituent	σ^*	E_s	σ_p
OCH_3	-0.39	+0.99	-0.27
CH_3	-0.17	0.00	-0.17
H	0.00	-	0.00
Cl	+0.20	+0.18	+0.28
Br	+0.21	+0.00	+0.23
I	+0.21	-0.20	+0.28

(d) THE ISOKINETIC RELATIONSHIP

For many reaction series, a plot of ΔH^* against ΔS^* is linear [41]. This is not altogether surprising, since many factors which affect ΔH^* would tend to exert a rate compensating effect on ΔS^*. For example, an electron withdrawing ortho substituent in basic ester hydrolysis lowers ΔH^*, and the increased solvation it produces also lowers ΔS^*. Steric strain and steric inhibition of solvation tend to counteract each other in a similar fashion.

A linear plot of ΔH^* against ΔS^* implies that

$$\Delta H^* = \beta \Delta S^* + \text{const.},$$

where β is the slope of the line.

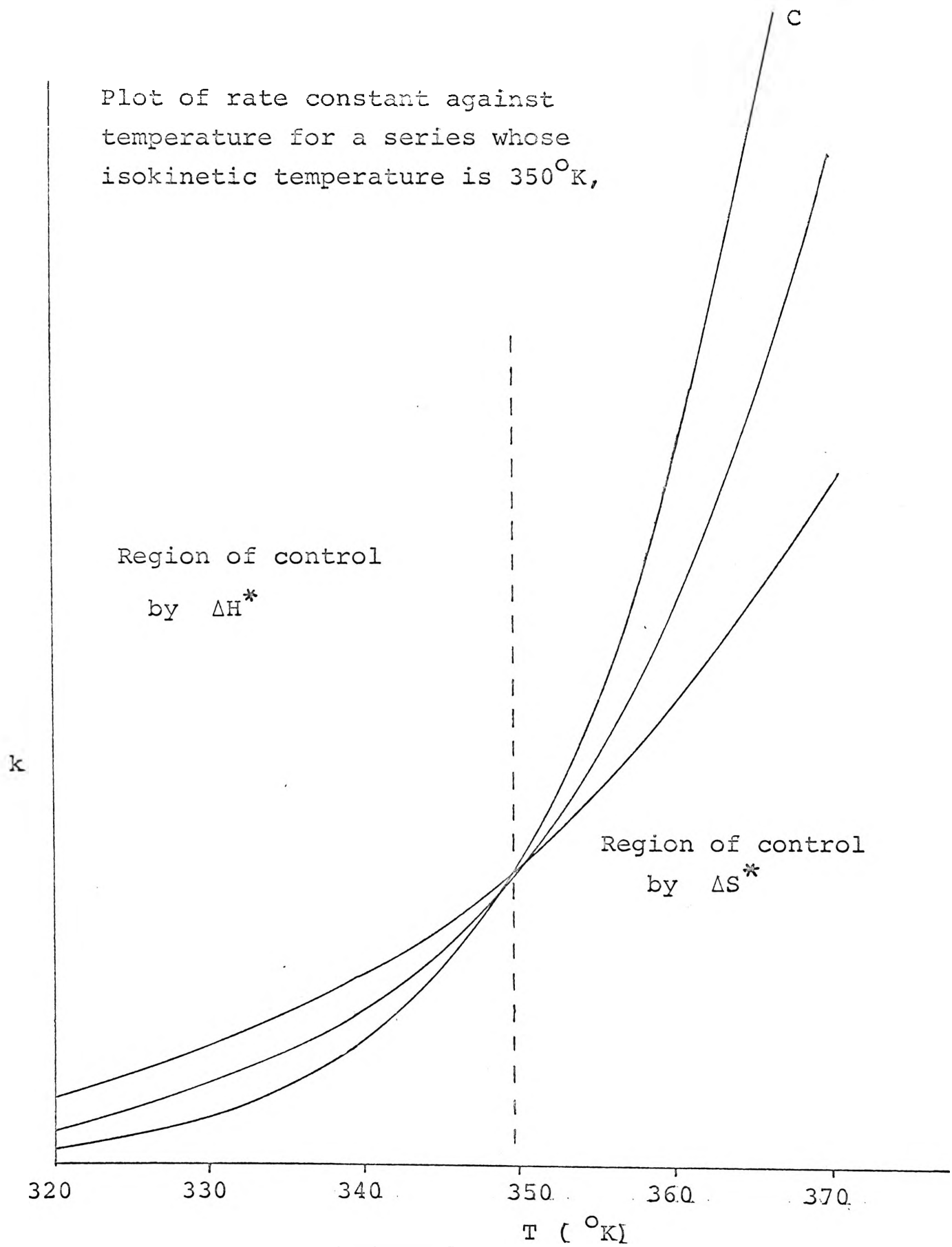

C
Plot of rate constant against temperature for a series whose isokinetic temperature is 350°K,
Region of control by ΔH*
Region of control by ΔS*
k
320
330
340
350
360
370
T (°K)

FIGURE 1

For two points on the line designated by the subscripts 1 and 2,

$$\Delta H_2^* - \Delta H_1^* = \beta (\Delta S_2^* - \Delta S_1^*),$$

that is,

$$\delta\Delta H^* = \beta \delta\Delta S^* . \quad \ldots\ldots \quad (19)$$

From the relationship

$$\Delta G^* = \Delta H^* - T\Delta S^*,$$
$$\delta\Delta G^* = \delta\Delta H^* - T\delta\Delta S^* .$$

Substituting from equation (19),

$$\delta\Delta G^* = \underset{(\delta\Delta H^*)}{\beta \delta\Delta S^*} - T\delta\Delta S^* \quad \ldots\ldots \quad (20)$$

Equation (20) shows that when T equals β the free energies of activation ΔG_1^* and ΔG_2^* are equal, and theoretically both reactions would proceed at the same rate. Leffler called the temperature β the isokinetic temperature.

As illustrated in Figure 1, the isokinetic temperature is a point of inversion of relative reactivities within a series. A reaction which is the slowest in a series below the isokinetic temperature is the fastest above it. In comparing the effects of structure and solvent on reactivity it is therefore important to consider rates at more than one temperature.

From equation (20) it can be seen that when T is less than β, the relative magnitudes of free energy of activation follow those of the enthalpy of activation, but when T is greater than β entropy of activation exerts the major effect on free energy, and hence reaction rate.

Various properties have been postulated for series that have an isokinetic point. Leffler [42] has pointed out that a linear enthalpy-entropy relationship indicates that all compounds in the series react by the same mechanism.

Brown and Newsom [43,44] attempted to rationalise reaction series on a linear free energy basis by drawing lines of constant slope (β = 310°K) through sets of points, and considering the distances between the lines as substituent contributions to free energy. Their conclusions may be criticised on the grounds that the linearity displayed by many of their reaction series may have been caused by random errors in measurement. Random error tends to be distributed along a line whose slope is the experimental temperature.

Exner [45] has suggested a method for indicating a true isokinetic relationship by considering the variation of rate constants rather than activation parameters, and this method will be discussed later.

Alkaline hydrolysis reactions of substituted benzoic esters have been shown to obey the isokinetic

relationship [41,45].

(e) THEORY OF ULTRAVIOLET ABSORPTION SPECTRA

(i) Electronic Transitions

Molecular species are capable of absorbing electromagnetic radiation in the ultraviolet region of the spectrum by electronic excitation. Ultraviolet absorption produces excitation of bonding or non-bonding electrons, and the wavelength at which the absorption takes place is governed by the energy of the electronic transition being observed, i.e. the energy difference between the electronic ground state and the level to which the electron is excited.

In molecular orbital terms, the major transitions involve excitation of electrons in σ- and π bonding orbitals to higher unoccupied bonding orbitals, or to antibonding orbitals. In addition to this, non-bonding electrons in atomic orbitals may be excited to bonding or antibonding molecular orbitals.

The intensity of the absorption observed for a particular transition depends on the quantum mechanical probability that the transition can take place. A transition which is "allowed" from symmetry considerations will produce strong absorption, and a "forbidden" transition will produce absorption of low intensity.

Because electronic energies in molecules are

affected by distributions in rotational and vibrational energy levels, their absorption spectra do not exhibit discrete frequency patterns, as do atomic spectra, but appear as diffuse bands or peaks. The number of peaks obtained in the spectrum of a chromophore depends on the complexity of its structure and the multiplicity of the transitions available to it.

(ii) The Beer-Lambert Law

The intensity of absorption of monochromatic radiation by a species is related to concentration by the Beer-Lambert equation.

$$\log \frac{I}{I_o} = \varepsilon cd, \qquad \ldots\ldots \quad (21)$$

where I_o and I are the intensities of incident and transmitted light respectively, c is the concentration of the species in moles per litre, d is the path length of the abosrbing solution in centimetres, and ε, the molar extinction coefficient, is specific to the species being examined.

The quantity $\log \frac{I_o}{I}$ is defined as the absorbance of the solution (A), and equation (21) becomes

$$A = \varepsilon cd.$$

(iii) UV Spectra of Substituted Benzenes

The benzene chromophore absorbs in three bands which are listed in Table 2. These bands are all produced

by excitation of delocalised π electrons in the benzene ring [46].

TABLE 2

Absorption Maxima of Benzene

λmax. (millimicrons)	εmax.
180	60,000
200	7,400
254	204

Of these, the band at 254 mμ is the most accessible for measurements in the liquid phase.

When a substituent is introduced in the benzene ring, two effects are observed. The first is that the energy levels of the benzene electrons are altered, both by the inductive and resonance properties of the substituent. An electron releasing substituent tends to increase the electronic energy level of the ring [47], causing a red (bathochromic) shift in the benzene spectrum, and increasing the intensity of the absorption. An electron withdrawing substituent has a less predictable effect. Its inductive effect serves to lower the electronic energy level. But most electron withdrawing substituents are capable of conjugating with the benzene ring, producing an increase in length of the conjugated system which lowers the gap between the highest occupied and lowest unoccupied energy levels. The resultant spectrum may

or may not exhibit a bathochromic shift relative to benzene, but the intensity of absorption in the higher bands is once again increased.

The second substituent effect results from the asymmetry produced in the benzene ring. The 0→0 transition (transition from electronic ground state to the ground state level in the electronic excited state) is forbidden in benzene, but appears as a weak peak at longer wavelengths in many mono-substituted benzenes, e.g. $\lambda_{max.}$ = 264 mμ, $\varepsilon_{max.}$ = 190. Substituents which interact strongly with the benzene ring, e.g. nitro, do not produce this transition [48].

Disubstituted benzene rings exhibit the effects of both substituents additively if the substituents do not resonate with the ring. If the substituents are capable of interaction with the ring, their effects on the spectrum may cancel each other [49].

(iv) Solvent Effects

A reaction in which an ionic species is formed from a neutral substrate produces a blue (hypsochromic) shift, accompanied by a decrease in intensity of absorption. For example, the 0→0 transition in benzoic acid (273 mμ, ε = 970) shifts to 268 mμ, $\varepsilon_{max.}$ = 560 for benzoate ion in water. This effect is caused by increased solvation of the ionic species which lowers the electronic energy levels of the chromophore.

This effect applies in the saponification of substituted benzoic esters.

E X P E R I M E N T A L

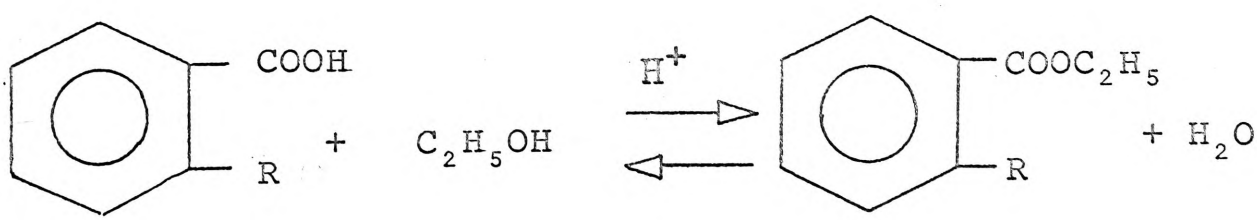
(a) PREPARATION OF ESTERS

In all, eight ortho substituted ethyl benzoate esters were prepared from the appropriate benzoic acid, the ortho substituents being acetyl, benzoyl, chloro, methoxy, nitro, phenoxy, phenyl and methyl groups. In addition, ethyl benzoate was available as laboratory stock, and was purified by vacuum distillation. Seven of the ortho substituted benzoic acids required for ester preparation were available commercially. The remaining one, o-phenoxybenzoic acid, was synthesised from o-chlorobenzoic acid.

Ortho benzoylbenzoic acid was available only as the monohydrate, and it was necessary to convert this into the anhydrous form before proceeding with the esterification.

For two esters trial batches were prepared, both from the acid chloride and via the Fischer-Speier esterification method. Both methods were found to give comparable yields, and the Fischer-Speier method was used for all esters.

(i) Fischer-Speier Esterification



The acid was refluxed with a four moles to one excess of ethanol for several hours. The excess of ethanol was necessary to force the equilibrium to the right. Concentrated sulphuric acid was used as the catalyst in the concentration of 3% by weight of the alcohol in the reaction [50].

On completion of refluxing unreacted acid was neutralised with sodium carbonate solution, and the lower ester layer was separated. The remaining aqueous layer was extracted twice with carbon tetrachloride, and the extracts added to the ester. The ester solution was washed twice with water, dried with anhydrous magnesium sulphate, and filtered. The carbon tetrachloride was evaporated, and liquid esters were purified by vacuum distillation. Solid esters were purified by recrystallisation from a 25% water-ethanol mixture.

The refractive index was used as a criterion of purity for liquid esters, and the melting point for solid esters. The physical constants of the esters are listed in Table 3.

TABLE 3

Physical Constants of the Esters Used

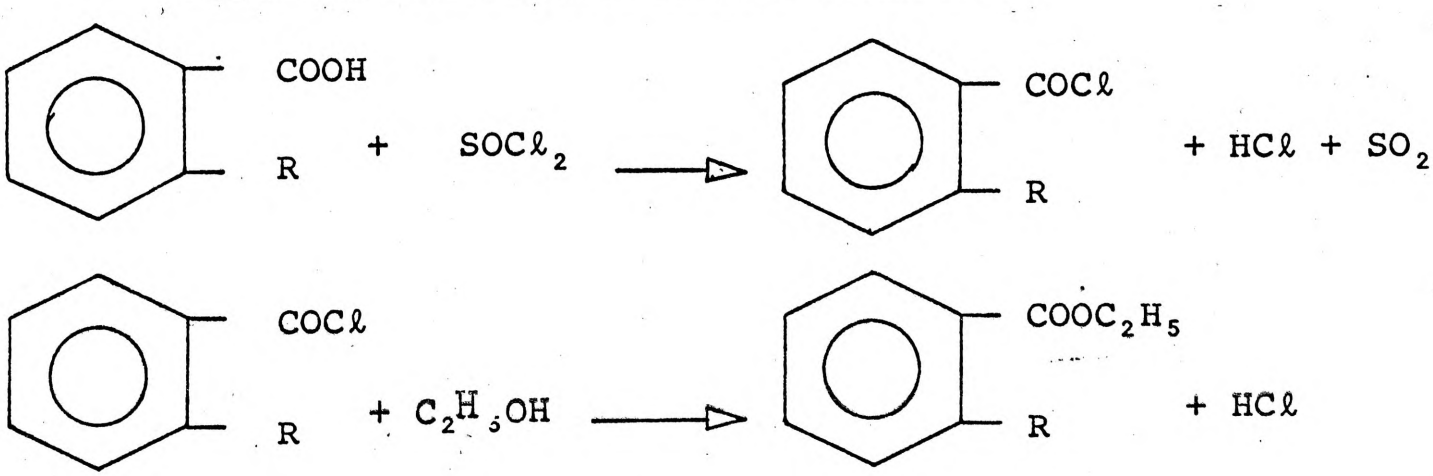
Ester	n_D^+ (observed)	n_D^+ (recorded)
ethyl o-acetylbenzoate	1.5138 (20)*	1.5122 (25)
ethyl benzoate	1.5062 (19)	1.505 (20)
ethyl o-chlorobenzoate	1.5219 (20)	1.522 (20)
ethyl o-methoxybenzoate	1.5220 (21)	1.524 (20)
ethyl o-phenoxybenzoate	1.5595 (24)	1.5646 (19)
ethyl o-phenylbenzoate	1.5728 (21)	1.5741 (17)
ethyl o-toluate	1.5082 (21)	1.508 (20)

	M.Pt.(observed)	M.Pt.(recorded)
ethyl o-benzoylbenzoate	58°C.	58°C.
ethyl o-nitrobenzoate	30°C.	30°C.

* Figures in brackets are the temperatures at which n_D was measured.

+ Refractive index relative to the sodium D line.

(ii) Esterification from the Acid Chloride



The acid was dissolved in benzene and refluxed with an excess of thionyl chloride (1.1 moles to 1) until hydrogen chloride evolution ceased. Excess thionyl chloride was distilled off, and the acid chloride was purified by vacuum distillation.

The acid chloride was packed in ice, and a 50% excess of ethanol was added dropwise from a dropping funnel. This was allowed to stand until evolution of hydrogen chloride ceased. The ester was purified by vacuum distillation.

(iii) Yields

Yields obtained were in the vicinity of 70% of the theoretical yield except for the o-benzoyl compound (30%), and the o-nitro compound (35%). The poor yield of the former ester was caused by the repeated recrystallisations necessary to obtain the desired degree of purity. The ortho nitrobenzoic acid was slow to esterify.

(iv) Preparation of Anhydrous o-Benzoylbenzoic Acid

The acid monohydrate was dissolved in benzene, separated from the aqueous layer, and dried with anhydrous magnesium sulphate. The solution was filtered and concentrated, and the acid was precipitated by addition of petroleum ether (b.p. 60-80°C.) to the hot solution, followed by cooling in ice. The melting point of the anhydrous acid obtained was 127°C. (Recorded 127-128°C.).

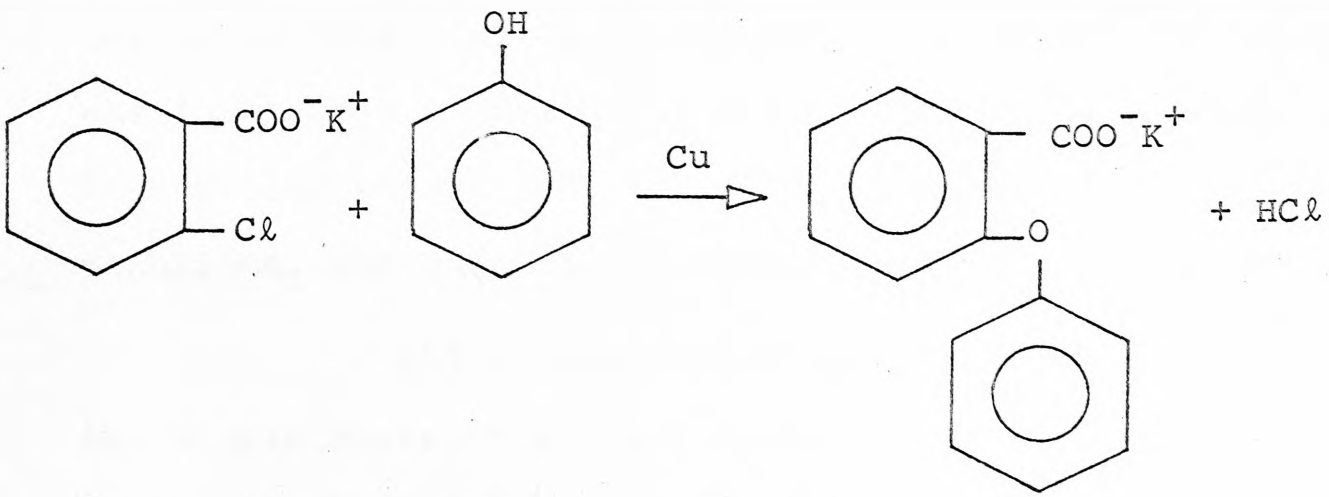
(v) Preparation of o-Phenoxybenzoic Acid

o-Chlorobenzoic acid was neutralised with potassium carbonate solution, and the potassium salt crystallised out and dried. Potassium o-chlorobenzoate (30 g.), phenol (21 g.), and copper powder (1.5 g.) was heated for

two hours in an oil bath at a temperature of 160-170°C. until the mixture became dark green.

This was extracted with dilute hydrochloric acid, neutralised with sodium carbonate solution, and filtered. The filtrate was extracted three times with ether to remove unreacted phenol, and the aqueous phase was acidified with concentrated hydrochloric acid and extracted twice with ether. The ether layer was dried with anhydrous magnesium sulphate, filtered, and evaporated. Light brown crystals of impure o-phenoxybenzoic acid were obtained.

The acid was purified by shaking with activated charcoal in benzene solution, evaporating the benzene, and recrystallising from 25% alcohol-water solution. The melting point was 114°C., in agreement with the recorded melting point.



(b) PURIFICATION OF DIOXAN

Kinetic studies carried out in dilute solutions of aqueous organic solvents are particularly prone to errors due to impurities in the organic component of the solvent. For this reason considerable care was taken in the purification of the dioxan used.

The initial method used for purification of dioxan was that described by Kraus and Vingee [51]. In this technique, commercial grade dioxan was refluxed for 6 hours with sodium hydroxide pellets and then distilled, the fraction distilling between 100-103°C. being collected. The dioxan so obtained was free of carbon dioxide and water. Its purity was tested by its refractive index.

$n_D^{20} = 1.4215$ n_D^{20} recorded = 1.4224

Since dioxan on standing is known to form peroxides which may be dangerously explosive [52,53], care was taken that it was never distilled down to a small volume. Poor yields (about 50%) of solvent were obtained by this technique, and two methods were used to improve on it.

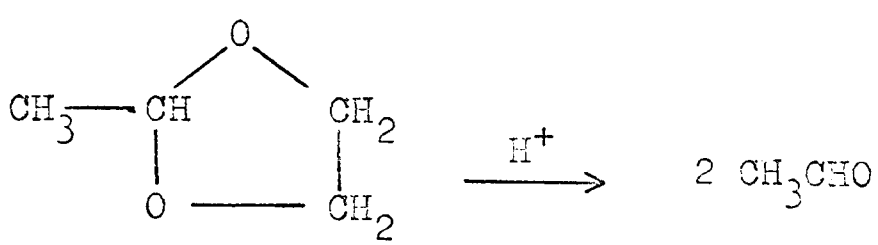
(i) A quantity of cyclohexanol was added to the dioxan during the first reflux. Cyclohexanol is high boiling (B.Pt. 161°C.) and non-azeotropic with dioxan [54], and acts as a "chaser" during distillation. It dilutes residual high boiling perioxides in dioxan, and allows the

maximum quantity of dioxan to be distilled.

(ii) Stannous chloride was added to the first reflux[53,55]. Stannous ion reduces peroxides present in the dioxan, which may then be distilled in safety. It was found that the stannous ion caused some of the dioxan to be hydrolysed to ethanol during reflux. The yield improved to about 80% when the dioxan was shaken with stannous chloride, filtered, and then refluxed with sodium hydroxide.

Later in the project kinetic difficulties were encountered (see page 60), which were traced to the presence of glycol acetal (2-methyl-1, 3-dioxolane) in the solvent, and methods[52,55-8] were examined to eliminate this impurity.

Commercial dioxan was shaken with stannous chloride and filtered. It was then refluxed with 1N hydrochloric acid (110 ml. per litre of dioxan) for 12 hours. The reflux was carried out in a stream of oxygen-free nitrogen, which acts as a carrier gas for acetaldehyde formed when glycol acetal is hydrolysed.



The dioxan was cooled, saturated with potassium hydroxide pellets, and decanted from the resulting aqueous

layer. It was again saturated with potassium hydroxide to remove water, and then refluxed for 12 hours over sodium metal, which was replenished from time to time. When all the water had been removed from the dioxan the sodium remained bright, and the dioxan was distilled under anhydrous conditions. A good yield (about 80%) of dioxan of boiling point 101-102°C. was obtained, and this was stored under nitrogen.

The dioxan had the following physical constants:-

m.pt. 11.8°C. n_D^{21} 1.4221

Recorded:- 11.8°C. n_D^{20} 1.4224 [53].

Since dioxan vapor is toxic, all operations were carried out in a fume cupboard.

PREPARATION OF SOLVENT

The solvent used, 60% w./v. dioxan/water was prepared by mixing 58 ml. of dioxan (density = 1.034 $g.cc^{-1}$ at 20°C.) with 42 ml. of water. The water used was distilled, and deionised by passing it through a "Deminrolit Mark VII" deioniser. It had an average conductance of 0.6 micromho/cm.

(c) KINETIC TECHNIQUES

In 1866, the following observations concerning kinetic methods were made by Harcourt and Esson [59]

> 'Although unquestionably every chemical reaction is governed by certain general laws relating to the quantity of the substances partaking in it, their temperature and physical state, and the time during which they are in contact, yet the number of cases in which the investigation of these is practicable is extremely limited. In the first place, it must be possible both to start and terminate the reaction abruptly at a given moment. In the next, either some product or some residue of the action must be a substance for whose estimation exact and ready methods are known so that the amount of change may be quantitatively determined. Lastly, all the conditions of the reaction must be measurable, or at least definable, and some of them susceptible of modification at will, that thus the influence of each may be examined'

(i) Techniques Used to Study Alkaline Ester Hydrolysis

The alkaline hydrolysis of ethyl benzoates has been studied classically by use of titration techniques [43,60-64]. These reactions are established as second order overall [65], first order with respect to both the ester and the hydroxyl ion concentrations. Computation of results can be simplified by using equal concentrations of ester and hydroxyl ion initially [62], and treating the reaction as second order with respect to one component (see page 3).

The reaction can be carried out in a bulk solution, with aliquots of approximately 10% of the total reaction being withdrawn at regular intervals [43,61],

or a batch technique may be employed in which the reactants are mixed in small batches, the time of mixing noted, and the time at which a batch is quenched being noted [63].

The rate of hydrolysis of benzoic esters in acid medium is slow compared with the rate in alkaline medium. For example, Newling and Hinshelwood [66] report $k_{25°C.}$ for the acid hydrolysis of ethyl benzoate in 60% aqueous acetone as 1.29×10^{-7} l.mole^{-1}sec.$^{-1}$, and $k_{25°C.}$ for the alkaline hydrolysis of the same compound in the same solvent as 3.8×10^{-3} l.mole^{-1}sec.$^{-1}$. These figures illustrate a factor of about 10^4 in rates of basic to rates of acidic hydrolysis. This difference in rates justifies the usual technique of quenching the reaction with an excess of standard hydrochloric acid. Since hydroxyl ion is removed as the reaction proceeds, the progress of the reaction can be measured by back titration of the hydrochloric acid with standard sodium hydroxide solution.

Of the two titration techniques mentioned above, the method of extracting samples from a bulk reaction mixture has limitations. As samples are progressively removed from the mixture, the free volume in the reaction container increases, and with it solvent vaporisation. Vaporisation of solvent alters the reactant concentrations in the reaction mixture, and, in the case of a mixed solvent, preferential vaporisation alters the composition of the solvent mixture.

Each of these factors can effect the kinetics of the reaction [67-69].

The method of making up batches of the reaction mixtures in small separate containers overcomes this problem, and if the free space within a container is kept to a minimum, solvent vaporisation is minimised. This technique allows a reaction to be carried out under an inert atmosphere, such as nitrogen, more readily.

B.C. Chauncy [70] studied the rates of hydrolysis of ortho-substituted ethyl benzoates by a conductimetric technique. As the reaction removes hydroxyl ion from the mixture, its progress is followed by measuring the electrical resistance of the reaction mixture, which increases with time.

The hydrolysis of substituted benzoic esters has also been studied by spectrophotometric methods [67,71]. The progress of the reaction can be followed by measuring ultraviolet absorbance of the ester (decreasing) or the benzoate ion (increasing) with time. Since spectrophotometric methods can only be used with very low ester concentrations (about 10^{-4}M.), a large excess of hydroxyl ion is used, and the reaction obeys pseudo first order kinetics. Gorchakovsky and Finkelstein [71] used concentrations of sodium hydroxide as high as 0.5M.

Of the kinetic methods surveyed here, the

titration technique is most universally useful, being limited only by reactions which are very fast in solution, such as the hydrolysis of ethyl o-benzoyl benzoate [28].

(ii) Kinetic Techniques Used in this Project

The major technique used in this work was a spectrophotometric method. However, initially twelve exploratory kinetic runs were carried out on ethyl o-toluate using a titration technique. This method was discontinued in favour of the absorption technique because of the poor economy of using large quantities of dioxan solvent which had been laboriously refined (see page 32). The results obtained by the titration method were in good agreement with the results subsequently obtained by the spectrophotometric method.

(a) The Titration Technique

In this technique, solutions of ester and sodium hydroxide were prepared of equal concentration - approximately 0.1 M. These solutions were brought to reaction temperature in a thermostated, stirred water bath. Batches of reaction mixture were then made up by mixing 5 ml. of ester with 5 ml. of sodium hydroxide solution. The mixing was carried out with a pipette calibrated at 20°C. The time of mixing was taken as the time at which half the ester had run into the hydroxide solution. In the reaction mixture $[\text{ester}] = [OH^-] = 0.05M$.

The reactions were carried out in test tubes of

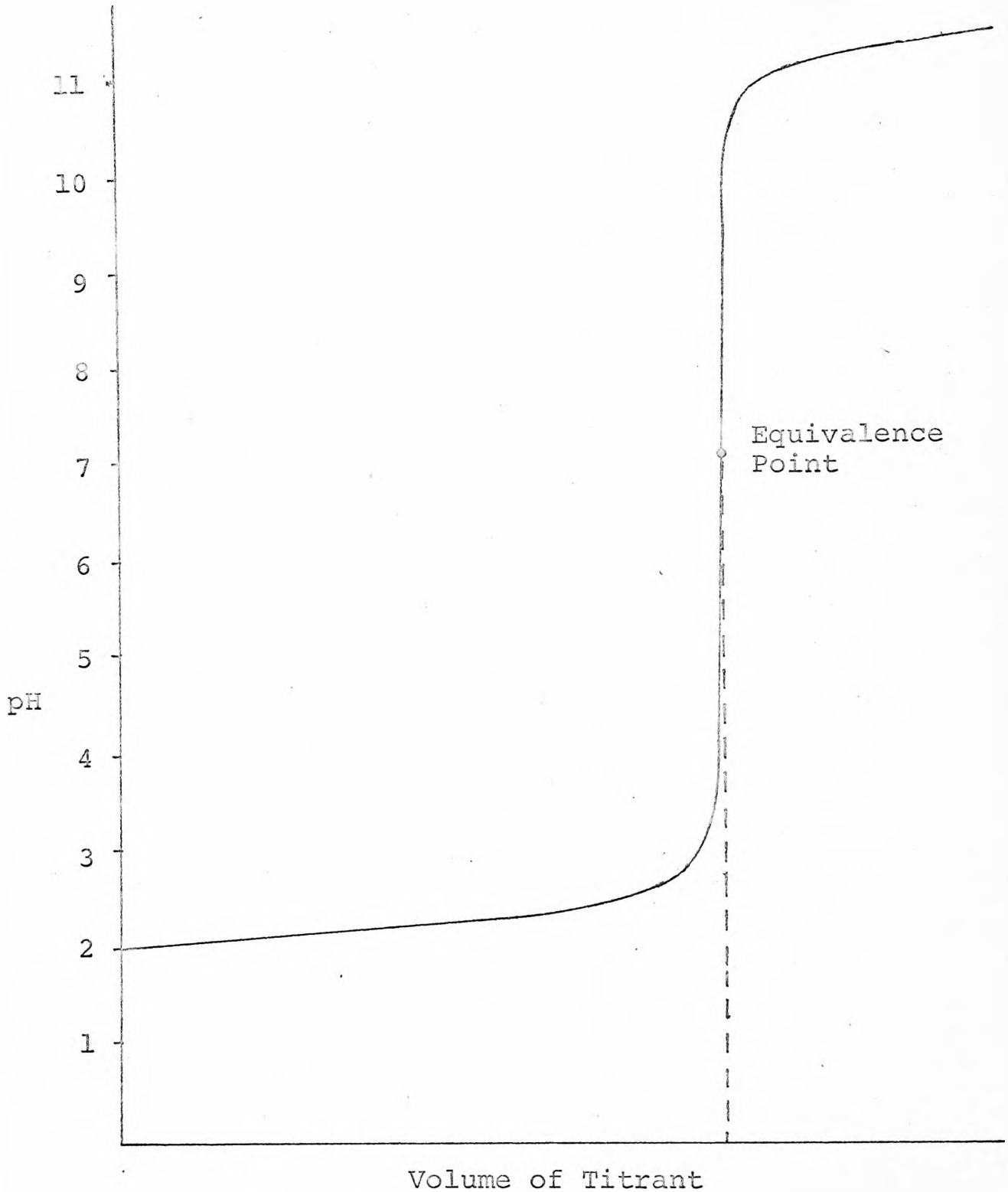


FIGURE 2

Titration of Strong Acid with Strong Base

15 ml. capacity to which ground-glass jointed caps could be fastened with stainless steel springs. The test tubes were sealed and clipped onto a support totally immersed in the water bath, ten batches being prepared for each run.

At suitable time intervals, the test tubes were removed from the water and poured into 5 ml. of standard approximately 0.1M hydrochloric acid. The concentration of hydroxyl ion in the batch was estimated by back titration of the quenched batch with standard sodium hydroxide solution.

The titrations were carried out with automatic titration apparatus consisting of a Radiometer TTT1(c) titrimeter, an ABU1(a) digital-reading autoburette, and an SBR2(c) 'TITRIGRAPH' recorder. The capacity of the autoburette was 2.5 ml., and the volume of titrant could be measured to within $\pm$0.002 ml. on a digital readout scale. The titration end-point was estimated by associating the digital readout with the pH-volume of titrant graph produced on the recorder (see Fig. 2). Since all titrations were strong acid-strong base type, the end-point was easily identifiable as the point of maximum inflection $\frac{\Delta pH}{\Delta v}$ of the curve. Reactions were followed for at least two half-lives.

(b) <u>The Spectrophotometric Technique</u>

As outlined later, problems were encountered with the absorbance method, and these brought with them variations in technique.

The reactions were carried out in 1 cm. quartz cells in an Optica CF4 ultraviolet/visible spectrophotometer. The ultraviolet source was a deuterium lamp, and all the reactions studied were monitored in the region 280-310 millimicrons.

The reaction temperature was maintained by pumping thermostated water through a brass block under the metal cell holder. The temperature in a cell could be monitored throughout the reaction by insertion of a thermistor probe attached to a Digitec digital thermometer, reading to 0.02°C. The water was pumped from a Tamson thermostat circulating bath whose heater was controlled by a Jumo electrical contact thermometer. To prevent the heater from overshooting the required temperature when operating near ambient, the Jumo was kept in a switching state by pumping refrigerated water through cooling coils inside the Tamson unit.

(iii) Preparation of Solutions

A bulk solution of carbonate-free concentrated sodium hydroxide was prepared with distilled de-ionised water [72] and stored in a polythene container.

Mixed dioxan-water solvent was prepared as described previously (see page 33). Sodium hydroxide solution of the required concentration was prepared by adding concentrated carbonate-free solution dropwise to the prepared solvent. The concentration of alkali used varied with the

temperature and the speed of the reaction, and for the compounds studied was in the range 0.01M to 0.2M. This involved addition of 2 to 40 drops of concentrated solution to 50 ml. of solvent.

The solution thus prepared was transferred to 20 ml. polythene medical dispensers, equipped with dropping nipples and screw caps. The solutions were standardised by mixing with an excess of standard hydrochloric acid, and titration with standard sodium hydroxide solution. The titrations were carried out with the autoburette as described on page 39.

The alkali solution thus prepared and standardised was introduced into 1 cm. quartz spectrophotometer cells from the polythene dispensers. The cells were filled almost to the top to minimise free space and solvent vaporisation, and stoppered with teflon stoppers. The cell to be used as a blank for absorbance measurements was also filled with alkali, and the solutions were then placed in the spectrophotometer with thermostated water circulating until a constant temperature had been achieved. The temperature of the central cell was monitored with the digital readout thermometer.

A concentrated solution of ester in aqueous dioxan was prepared, such that addition of one or two drops of this solution to the alkali in a cell produced an absorbance of about 0.7 at the wavelength used. Because of the low solubility of some esters, it was sometimes necessary to

prepare this solution with a higher proportion of dioxan.

The ester solution was added dropwise to the alkali solution at reaction temperature, and was allowed to stand until the reaction mixture had recovered any temperature loss caused by the mixing.

A minimum of twelve Time-Absorbance readings were taken during the reaction, and each run was followed for at least two half-lives (75%). Time was read to the nearest half-minute with a stopwatch, and the temperature of the monitored cell was kept constant to within 0.1°C. At the end of a run the temperatures of the other two cells were taken. At temperatures near ambient these were usually the same as the central cell, but at higher reaction temperatures these varied by as much as 0.2°C, depending on their positions within the cell compartment. The reaction temperature for these cells was taken as that finally measured.

(iv) Ultraviolet Absorption of Esters

Ultraviolet absorption spectra of the esters studied were measured with a Perkin-Elmer 137 UV continuous scan spectrophotometer. A solution of the ester in alkaline aqueous dioxan was prepared as described above, and the spectrum of this was measured against a blank of alkaline aqueous dioxan.

The esters were then saponified by heating the solution at 80°C. for two to three hours until the reaction

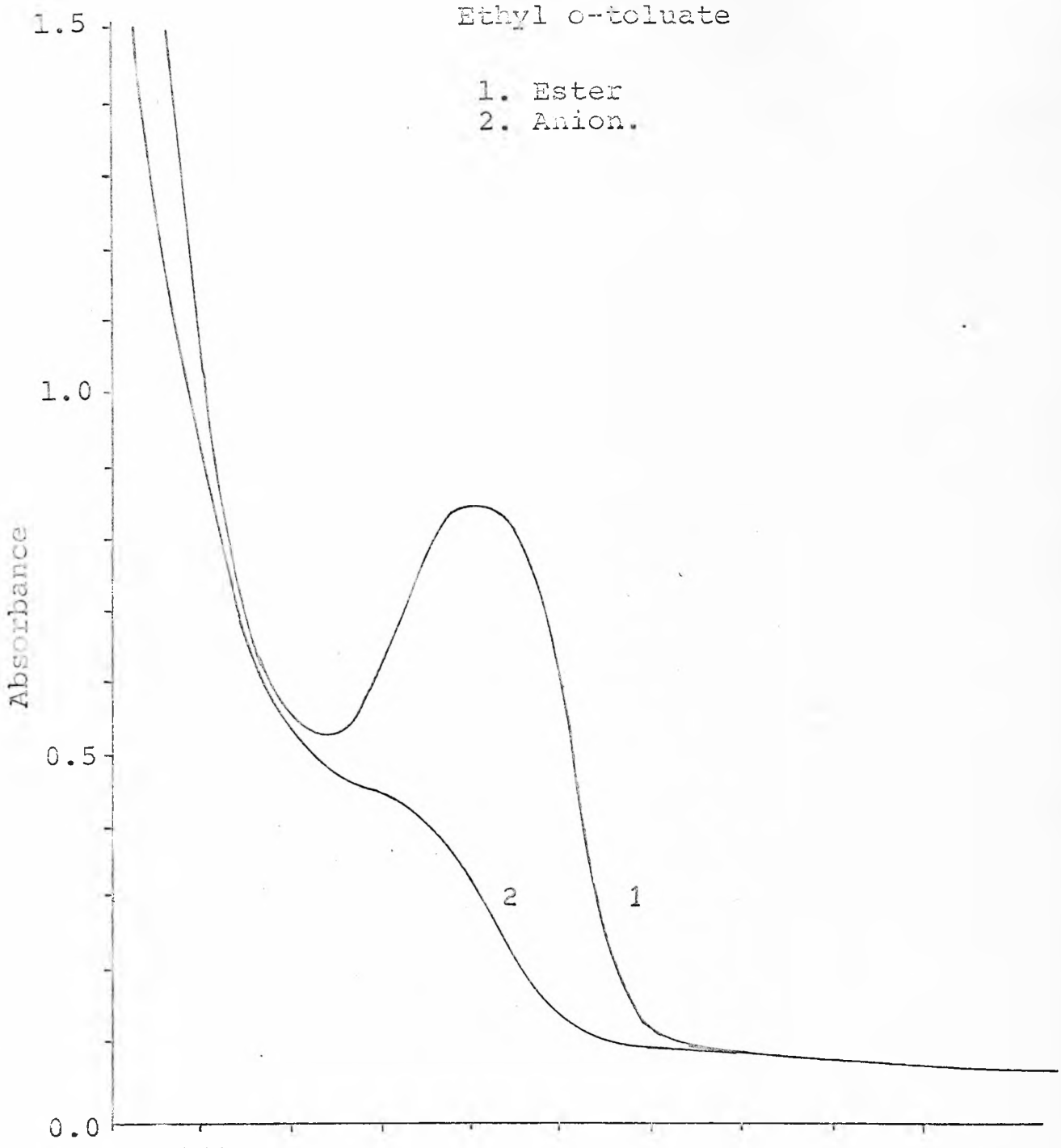
was complete. The blank alkaline solution was also heated to offset any absorption caused by solvent-alkali reaction (see page 62). The ultraviolet spectrum of the anion in solution was then recorded. Comparison of the spectrum of ester and anion in equal concentration showed that only four of the esters (see Table 3) produced peaks which were suitable for studying concentration change during saponification. Of the remainder, four did not produce 0 ⟶ 0 transitions (Figs. 8-11), and the ester-anion spectra of ethyl benzoate overlapped too much to be suitable (Fig. 7). Ultraviolet spectra of the esters and their anions are recorded in Figures 3-11.

From the ester-anion spectra, a wavelength was selected at which absorbance was measured during kinetic runs. As far as possible, the selected wavelength was one at which there was no residual anion absorbance, but it was not altogether possible to avoid residual absorbance during all the runs (see page 74). Wavelengths at which esters were monitored are listed in Table 3.

TABLE 3

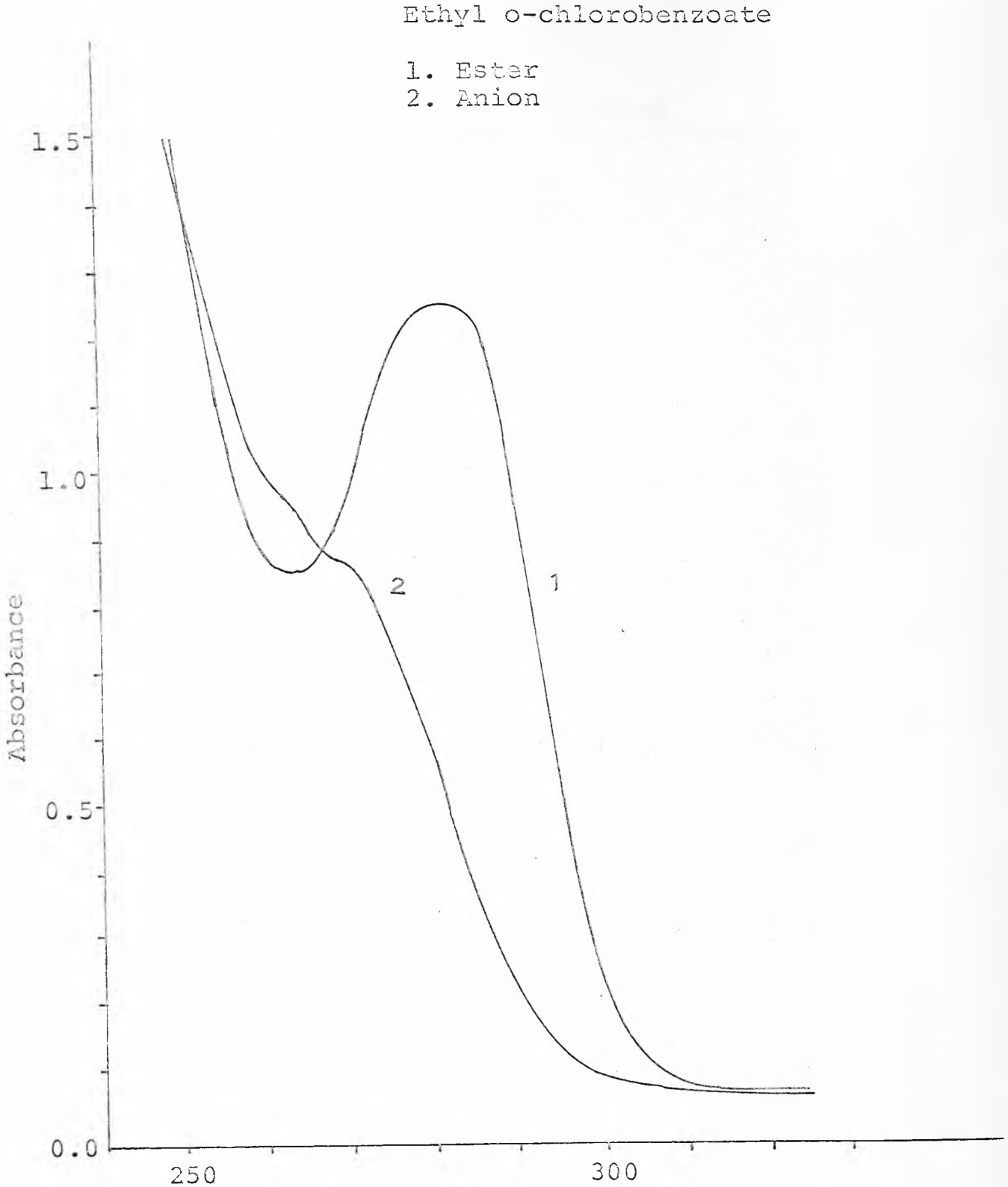
Wavelengths Used to Measure Concentration

Compound	Wavelength (mμ)
Ethyl o-toluate	290
Ethyl o-chlorobenzoate	293
Ethyl o-methoxybenzoate	310
Ethyl o-phenoxybenzoate	300



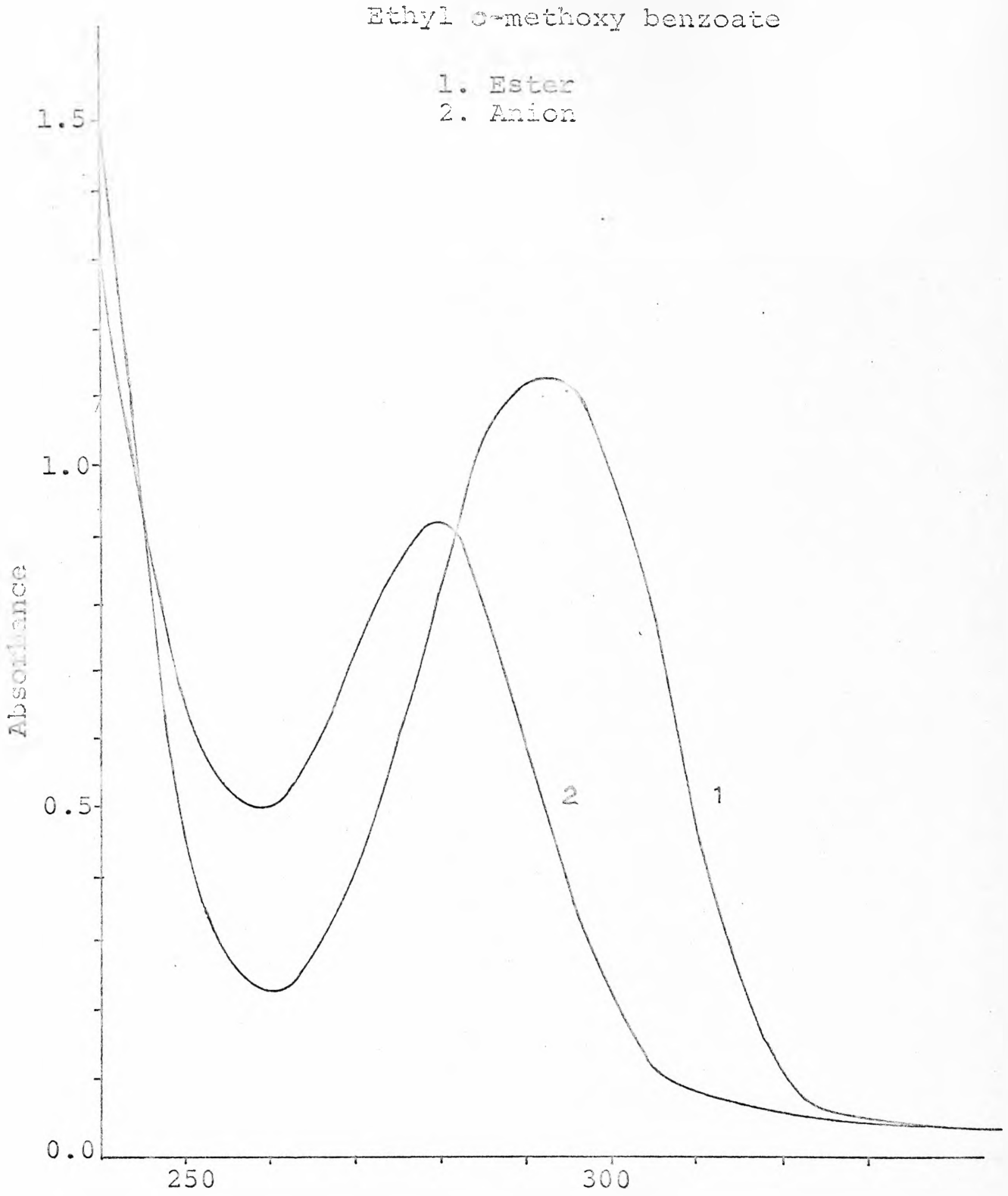
UV Spectrum of Ethyl o-toluate

FIGURE 3



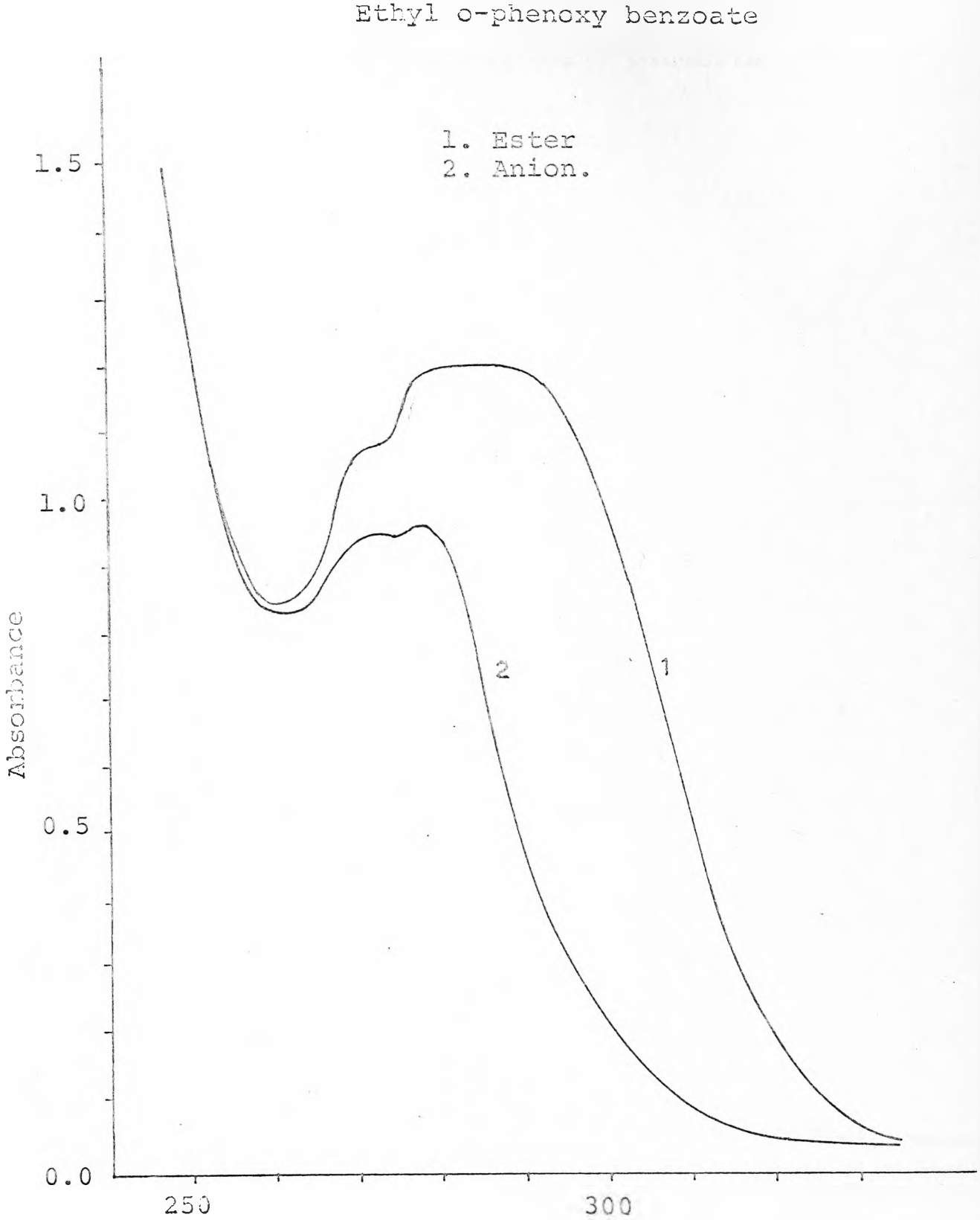
UV Spectrum of Ethyl o-chlorobenzoate.

FIGURE 4



UV Spectrum of Ethyl o-methoxy benzoate

FIGURE 5



UV Spectrum of Ethyl o-phenoxy benzoate

FIGURE 6

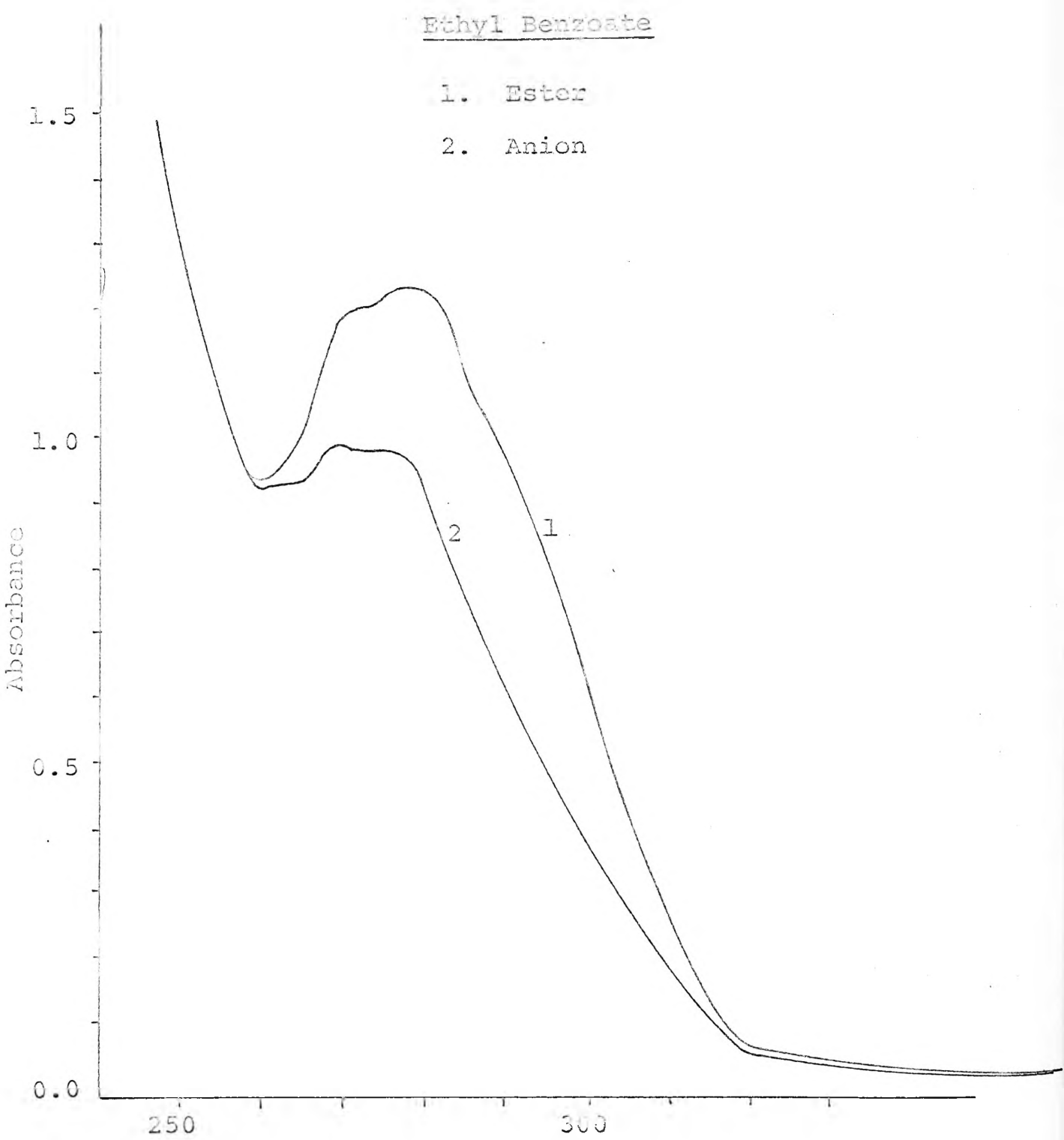

Ethyl Benzoate
1. Ester
2. Anion
1.5
1.0
0.5
0.0
Absorbance
1
2
250
300
Wavelength (millimicrons)

FIGURE 7

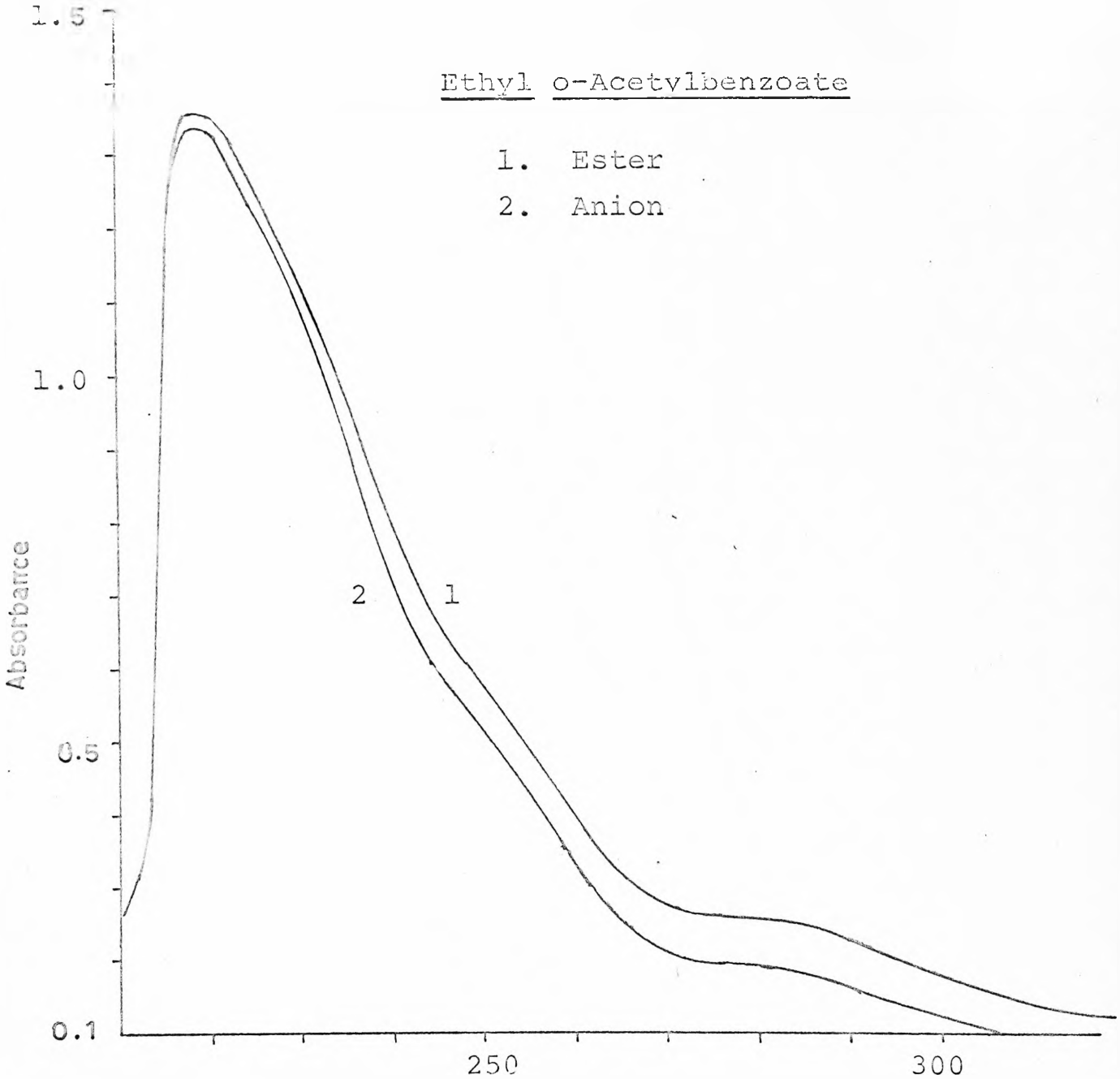

Ethyl o-Acetylbenzoate
1. Ester
2. Anion
1.5
1.0
0.5
0.1
Absorbance
2
1
250
300
Wavelength (milli microns)

FIGURE 8

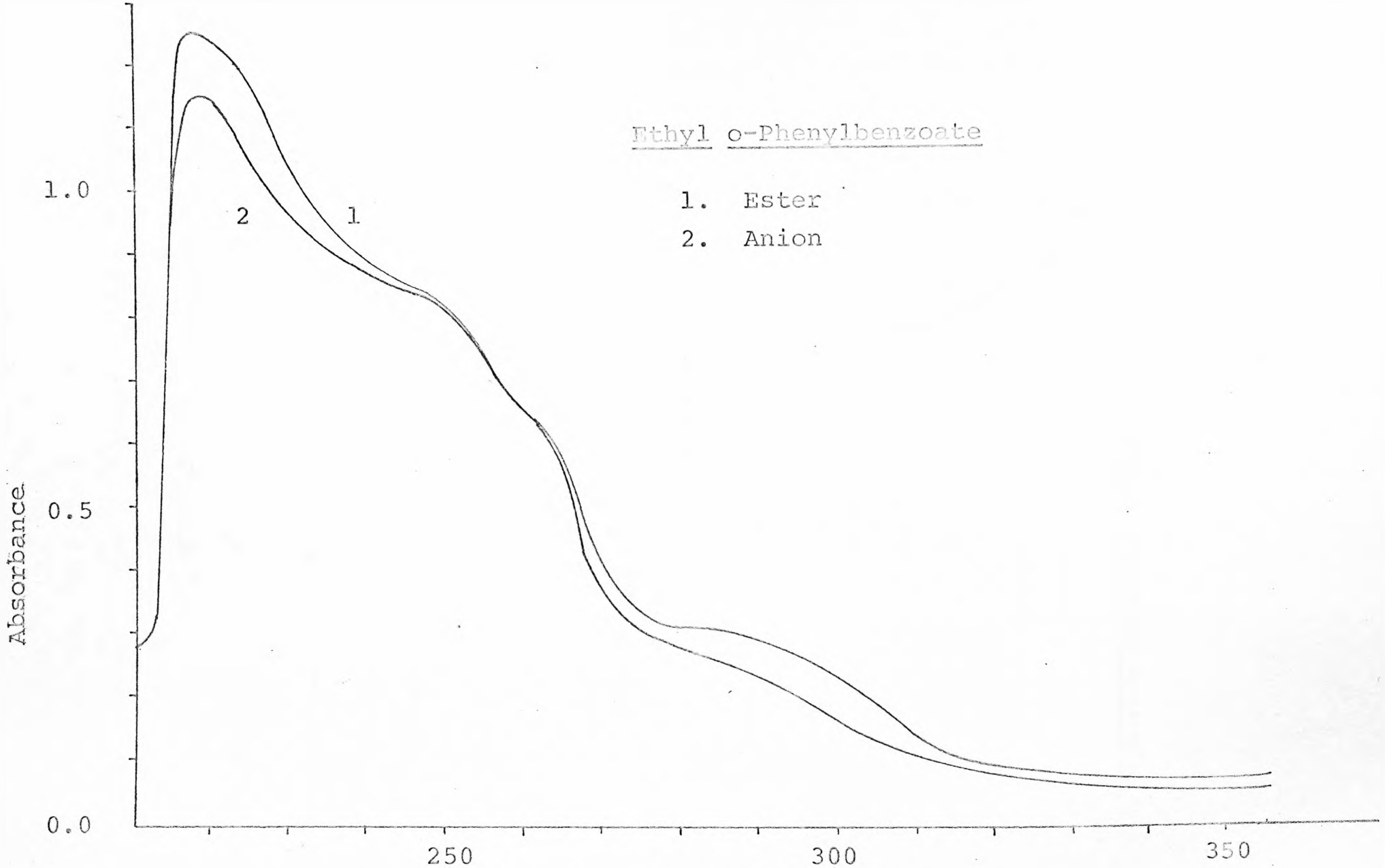

Ethyl o-Phenylbenzoate
1. Ester
2. Anion
1.0
0.5
0.0
Absorbance
2
1
250
300
350
Wavelength (millimicrons)

FIGURE 9

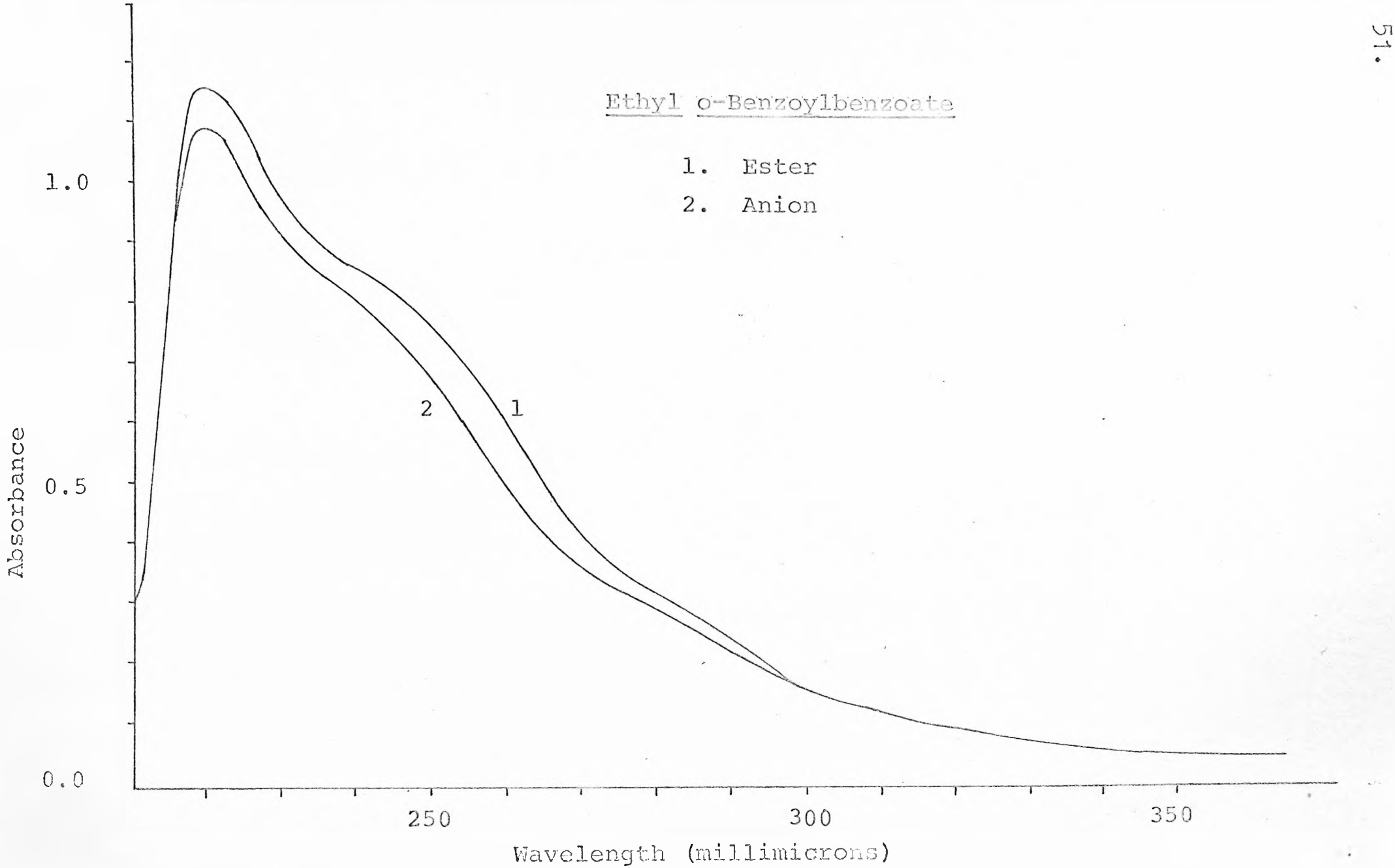

Ethyl o-Benzoylbenzoate
1. Ester
2. Anion
1.0
0.5
0.0
Absorbance
2
1
250
300
350
Wavelength (millimicrons)

FIGURE 10

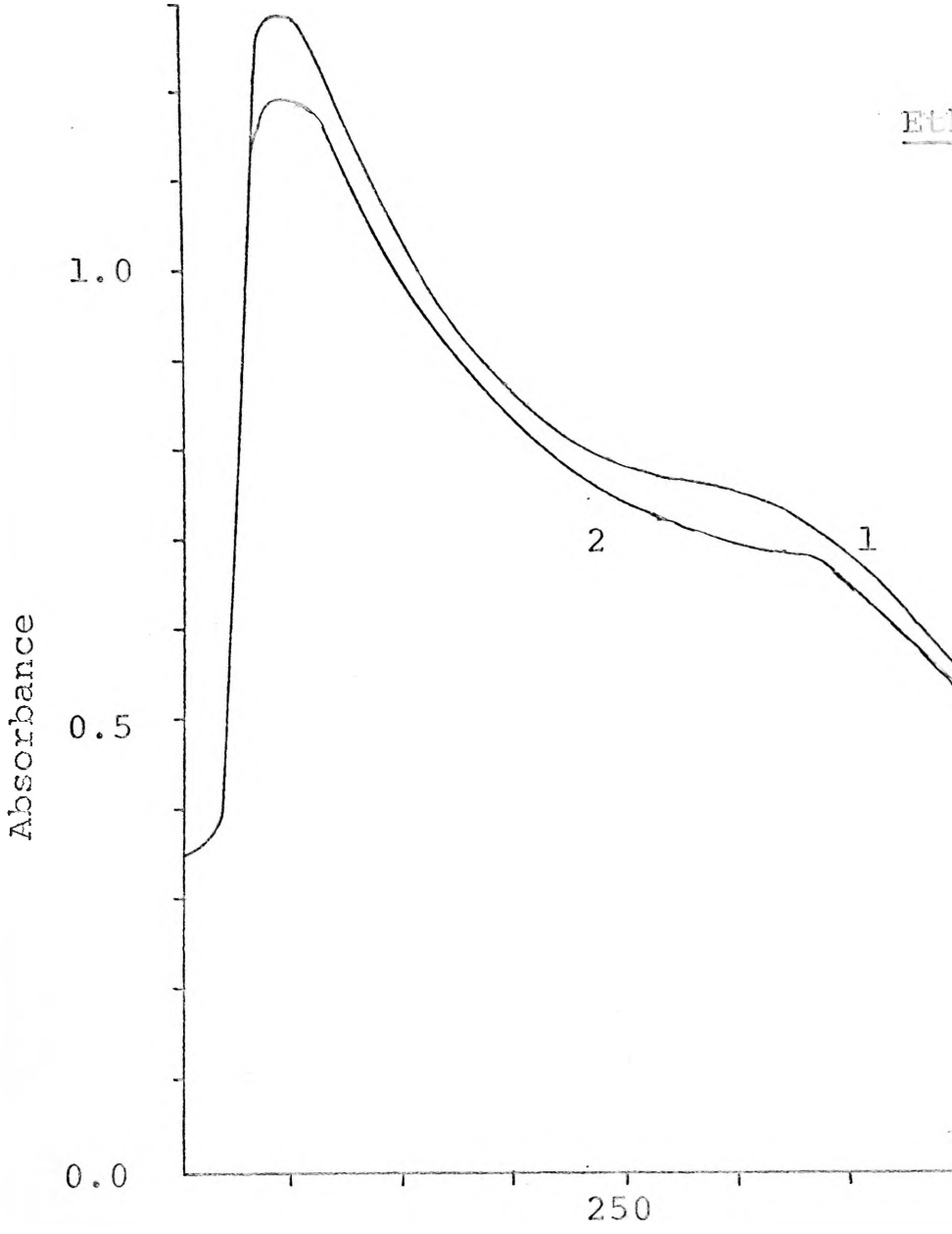
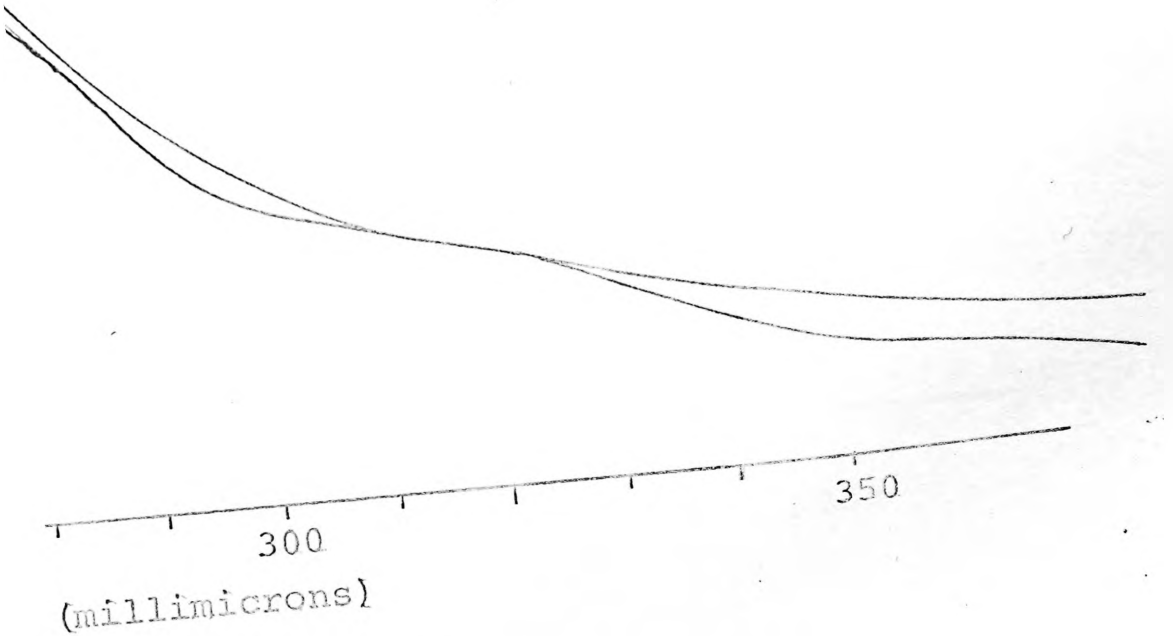


FIGURE 11

hyl o-Nitro benzoate

1. Ester

2. Anion



(d) COMMENTS ON EXPERIMENTAL TECHNIQUE

(i) Preparation of Solutions

The method used for preparation of the alkaline catalyst solution (see page 40) introduces slight variations in the solvent composition, since concentrated aqueous sodium hydroxide solution is added dropwise to the prepared 60% dioxan-water solvent. At the maximum concentration used (0.2M), the volume of concentrated aqueous alkali added is less than one percent of the solvent, and it is considered that this variation would not have a significant effect on the rate constant [28].

A saturated solution was used to avoid carbonate contamination of the alkali, and it was not feasible to saturate the mixed solvent with sodium hydroxide, since this would cause dioxan to come out of solution.

As described above (see page 42), the ester was introduced dropwise into standardised alkaline aqueous dioxan in the cells. The assumption made is that the addition of one drop of ester solution (about 0.02 ml.) to a 3 ml. cell of standardised sodium hydroxide solution has a negligible effect on the concentration of the solution. The error introduced would be less than one percent, and this was considered to be acceptable. The advantages of this technique are twofold:-

(1) The concentration of ester in the cell can be readily

adjusted by altering the concentration of the bulk ester solution. Since the reaction is first order with respect to the ester (see page 71) and zero order with respect to the relative excess of hydroxyl ion, the rate constant is independent of initial ester concentration.

(2) This technique avoids unnecessary exposure of solutions to the air, with the associated risk of carbon dioxide absorption. Absorption of carbon dicxide lowers the concentration of hydroxyl ion in the solution, and introduces error into the rate constant.

(ii) Standardisation of Sodium Hydroxide

The method of mixing a solution sample with excess hydrochloric acid, and back titrating with sodium hydroxide, was employed because the autoburette was being used for other titration work, and it was not practical to change the solutions for a small number of runs. It was desirable to use the autoburette for standardisation, as this allowed more economical use of solutions.

While the method of back titration introduces additional sources of error, the results obtained in standardising solutions were extremely consistent, the titrations in most cases being reproducible to one thousandth of a millilitre.

(iii) Carbon Dioxide Contamination

The overall hydrolysis rate is proportional to

the concentration of hydroxyl ion in the solution.

$$\text{Rate} = k\,[OH^-]\,[\text{Ester}]$$

If the alkali solution has been allowed to absorb carbon dioxide from the air, the rate constant obtained will be lowered.

$$2OH^- + CO_2 \longrightarrow CO_3^{2-} + H_2O$$

Some research workers (e.g.Chapman [62]) take the precaution of working under nitrogen to eliminate this problem. This is particularly relevant where a titration technique is used and the solutions are frequently exposed to the air, but it was not considered necessary for the present method.

Solutions were made from carbon dioxide free dioxan (see page 33) and freshly deionised water. The pure dioxan was stored under nitrogen, and measured from a two way burette whose air intake was filtered through soda-asbestos. Carbonate-free sodium hydroxide solution was used to make up alkali solutions which were then stored in polythene dispensers, and the solution was fed from the dispensers into the cells, which were stoppered.

Since the spectrophotometric technique does not involve constant re-exposure of the reaction mixture to the air, it was considered that the opportunities for absorption of carbon dioxide had been physically minimised, and the reproducibility of rate constants using solutions of different hydroxyl ion concentration bears this out.

There were greater opportunities for solution-air contact when the solutions were standardised. Carbon dioxide absorbed at this stage would not affect the result of the standardisation, because the solution was reacted with an excess of hydrochloric acid which would also react stoichiometrically with any carbonate ion in the solution.

The hydroxide solution used in the autoburettes was protected from carbon dioxide by tubes of soda-asbestos.

(iv) Ester Concentration

The hydrolysis reactions were carried out with a large excess of hydroxyl ion over ester. The observed kinetics were pseudo first order with respect to ester, and pseudo zero order with respect to hydroxyl ion.

To calculate the specific rate constant for the reaction, the pseudo first order rate constant was divided by the hydroxyl ion concentration.

$$\text{Rate} = k_1 [\text{Ester}]$$

$$k_1 = k_2 [OH^-]$$

where k_1 = pseudo first order rate constant.

k_2 = specific rate constant for the reaction.

The above procedure assumes that the hydroxyl ion absorbed in the reaction

$$RCOOR' + OH^- \longrightarrow RCOO^- + R'OH$$

is negligible compared to the overall hydroxyl ion concentration,

which can be regarded as constant during the reaction.

The ester concentration was not measured accurately in preparing every run (see page 41), but in most cases it was about 10^{-4}M. If it is assumed that the maximum ester concentration is 2×10^{-4}M, and the lowest hydroxyl ion concentration used is 150×10^{-4}M, then the percentage of hydroxyl ion used in 75 percent of a reaction would be 1 percent of the original hydroxyl ion concentration. This is the maximum possible error which can be obtained by this approximation.

(v) Problems Involved in Temperature Control

As stated above (page 40), the reaction cells were heated by thermostated water pumped by the Tamson circulating heater through a brass block under the cell holder.

The reaction mixtures in the cells were probably subjected to temperature differentials within the mixture, as the only form of mixing within a cell would be that provided by natural convection, and the disturbances suffered when the cell holder was moved in taking readings.

Other problems related to temperature control were that it was not possible at higher temperatures to keep all cells in the compartment at the same temperature, that the temperature of a cell had to be maintained constant throughout the life of the reaction, and that the temperature

in a cell was a few degrees below the temperature set on the Jumo thermometer, and it was not easy to reproduce runs at exactly the same temperature.

The Digitec digital readout thermometer was used to monitor the temperature of one cell continuously during a run. If the temperature started to drift it was possible to regulate this drift by adjusting the switching temperature of the Jumo slightly, and by this means to keep the temperature of a reaction constant to within 0.1 of a centigrade degree.

Since it was undesirable to open the cell compartment during a run, the temperatures of the other two cells were measured at the end of each run, the assumption being made that if the temperature of one cell was maintained constant, then the temperatures of the other cells would also be constant.

Temperature control within a cell would have been improved with thermostated cells in which water was pumped through the actual cell walls, but these were not available.

TABLE 4

Effect of Curvature on Rate Constant

ETHYL O-TOLUATE 35.8 DEG C.

Absorbance	Time	Calc. Absorbance	Difference
.505	1530.00	.596	.009
.587	1860.00	.578	.009
.560	2280.00	.555	.005
.534	2760.00	.530	.004
.504	3330.00	.502	.002
.472	3900.00	.476	-.004
.452	4440.00	.452	-.000
.412	5280.00	.418	-.006
.388	5910.00	.393	-.005
.358	6750.00	.363	-.005
.330	7590.00	.336	-.006
.308	8370.00	.312	-.004
.284	9120.00	.290	-.006
.260	10350.00	.258	.002
.244	11070.00	.241	.003
.229	11640.00	.229	.000
.222	12300.00	.215	.007

k computed from these results = 0.8612E-03

k(36.2°C.) from more accurate results = 0.1082E-02

ETHYL O-TOLUATE 55.3 DEG C.

Absorbance	Time	Calc. Absorbance	Difference
.273	3270.00	.257	.016
.250	3810.00	.250	.010
.240	4500.00	.241	-.000
.226	5130.00	.233	-.007
.220	5760.00	.225	-.005
.206	6480.00	.216	-.010
.200	7350.00	.206	-.006
.193	8010.00	.199	-.006
.188	8940.00	.190	-.002
.184	9780.00	.181	.003
.179	10470.00	.175	.004
.172	11130.00	.169	.003
.167	11730.00	.164	.003

k computed from these results = 0.1139E-02

k(55.2°C.) from more accurate results = 0.4205E-02

(e) A PROBLEM WITH SOLVENT IMPURITY

The initial method used for dioxan purification was the method of Kraus and Vingee (see page 31). This method was chosen because it produced dry carbon dioxide-free dioxan, and it had previously been used successfully in studying reaction kinetics in aqueous dioxan [70].

Initial runs carried out on ethyl o-toluate and ethyl o-chlorobenzoate by the spectrophotometric technique produced curvature in the log A against time plot. The curvature produced was slight, but it was more pronounced at high temperatures than at low temperatures. Since the rate constants were calculated from the least squares slopes of these plots, the values so obtained were inaccurate, and the points did not fit on an ART (log $k/_T$ v's $1/_T$) plot. Two sets of data so obtained are listed in Table 4. It will be noted that the effect is more pronounced at the higher temperature than at the lower temperature, and that the values of k so obtained are lower than the true values.

Various refinements were introduced into the experimental technique, and it was found that when a solvent/alkali mixture was used as a blank instead of pure solvent the curvature was greatly reduced, indicating that the curvature may have been caused by absorbance produced in a reaction between the solvent and alkali during the course of

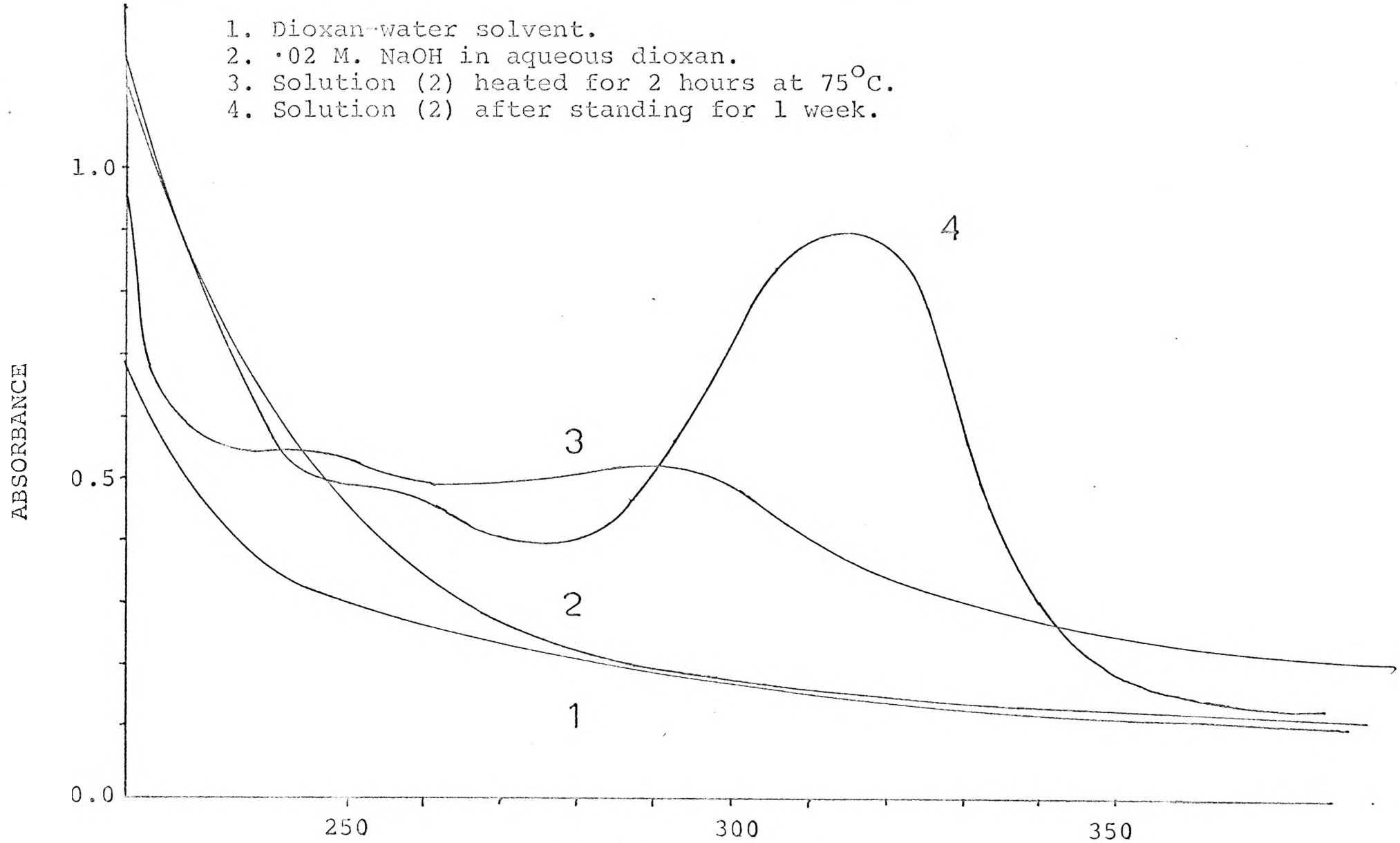

1. Dioxan-water solvent.
2. ·02 M. NaOH in aqueous dioxan.
3. Solution (2) heated for 2 hours at 75°C.
4. Solution (2) after standing for 1 week.
ABSORBANCE
1.0
0.5
0.0
250
300
350
Wavelength (Millimicrons)
1
2
3
4

FIGURE 12

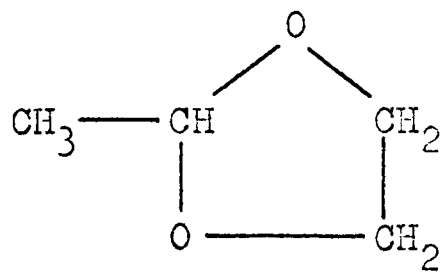
a run. This residual absorbance was not allowed for in the computation, and produced curvature in the results. It was possible to demonstrate that the remaining slight curvature was due to residual anion absorbance, as described later (see page 74), and this was computed out.

An investigation was carried out into the nature of the solvent/alkali reaction. It was found that if a fresh solution of sodium hydroxide in aqueous dioxan was prepared, and heated for a short while, the solution changed from being transparent to ultraviolet radiation in the region of measurement (280-310mμ) to absorbing in this region.

The absorption produced, and the wavelength of its peak, varied with the temperature to which it was subjected the time for which it was heated, and the concentration of the alkali used.

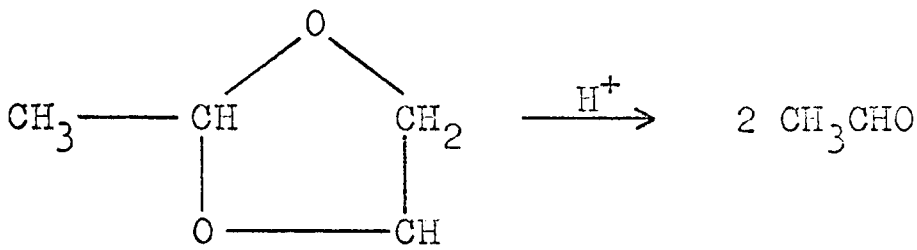
Figure 12 shows the spectra of a sample of (1) dioxan-water solvent (2) .02 molar sodium hydroxide in dioxan-water solvent (3) the solution (2) after heating for two hours at 75°C., and (4) the same solution after standing for one week at room temperature.

A known impurity in commercial dioxane is glycol acetal (2-methyl-1,3-dioxolane) [52,73]



2-methyl-1,3-dioxolane.

Glycol acetal is stable in the presence of alkali, but is readily hydrolysed in the neutral and acidic solution to acetaldehyde [73].

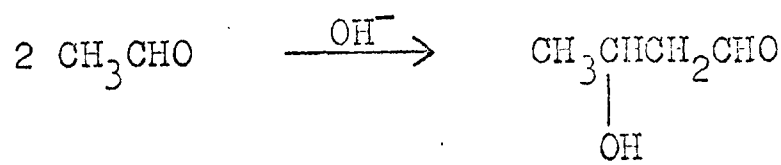


In the Kraus and Vingee method of purification, dioxan is refluxed with sodium hydroxide and sodium. This treatment does not hydrolyse glycol acetal present in the dioxan.

When dioxan is diluted in aqueous solution, glycol acetal present can hydrolyse to acetaldehyde. The solution is then made alkaline and heated during the kinetic runs.

Acetaldehyde absorbs ultraviolet strongly at 180 mμ and gives a very small peak ($\varepsilon = 12$) at 293 mμ [74,75]. However, the absorption at 293 mμ is not sufficient to account for the absorption illustrated in Figure 12.

When acetaldehyde is heated in the presence of alkali, it readily undergoes an aldol condensation reaction [76,77].



aldol

The aldol dehydrates on heating to unsaturated crotonaldehyde.

$$CH_3CH(OH)-CH(H)CHO \xrightarrow{-H_2O} CH_3CH = CHCH = O$$

crotonaldehyde

On further heating with alkali, the reaction can proceed further to produce long chain conjugated aliphatic compounds.

$$CH_3CHO + CH_3CH = CHCHO \xrightarrow[-H_2O]{OH^-} CH_3 (CH = CH)_2 CHO$$

2,4 - hexadienal

$$CH_3 (CH = CH)_2 CHO + CH_3CHO \xrightarrow[-H_2O]{OH^-} CH_3 (CH = CH)_3 CHO$$

2,4,6 - octatrienal

Progressive chain lengthening of these conjugated compounds produces a bathochromic shift in their wavelength of maximum absorption. The increase in wavelength appears in conjunction with a sharp increase in intensity of the major K-band peak, produced by $\pi \longrightarrow \pi^*$ electronic transitions [78].

The absorption characteristics of the compounds mentioned above are listed in Table 5.

TABLE 5

Absorption Maxima of Polyene Aldehydes [79]

	K-band		R-band	
	λmax(mμ)	εmax	λmax(mμ)	εmax
Crotonaldehyde $CH_3CH = CHCH = O$	217	15,650	320	19
2,4-hexadienal $CH_3(CH=CH)_2CH = O$	271	25,000	366	30
2,46-octatrienal $CH_3(CH=CH)_3CH = O$	315	37,000	380	28

Solvent : Ethanol

The molar extinction coefficients for the minor R-band peaks are insignificant in comparison with the peaks in the K-band.

It is hypothesised that the absorbance produced when an alkaline solution of aqueous dioxan was heated, and illustrated by spectra (3) and (4) in Fig. 12, was due to the formation of condensed conjugated unsaturated aldehydes in the solution. The absorbing species could be produced by hydrolysis of glycol acetal, an impurity in dioxan, and successive condensations of the acetaldehyde so formed in the presence of hydroxyl ion.

Spectrum (4) in particular possesses a decisive peak at a wavelength of 315mμ, which corresponds to the major peak of 2,4,6-octatrienal. Its major absorbance is 0.7, and applying this and the stated extinction coefficient ε= 37000

to the Beer-Lambert equation $C = \frac{A}{\varepsilon d}$,

this absorbance would be accounted for by a concentration of 2×10^{-5}M. octatrienal.

The May and Baker commercial dioxan used has been shown by Irving and Mahnot [80] to contain glycol acetal as an impurity of 1%. If the impurity at this level was completely converted to 2,4,6-octatrienal in 60% dioxan, the concentration produced would be about 4×10^{-2}M., which indicates that the concentration noted above could easily result under non-optimal conditions.

As indicated on page 74, a final absorbance as low as 0.01 is sufficient to affect the results of this technique, so that any small concentration of a highly absorbing species would account for the difficulties encountered.

The method previously used for purifying dioxan was abandoned, and the method described by Fieser and others, and outlined on page 32 was adopted. This involved an initial refluxing of dioxan with hydrochloric acid to hydrolyse glycol acetal to acetaldehyde. The acetaldehyde is removed as a vapor by a carrier stream of nitrogen during the reflux.

When this method of purification was applied, considerable quantities of acetaldehyde were detected in the vapor. A fresh dioxan solution of sodium hydroxide was submitted to heat for 2 hours at 75°C., and the absorbance produced was much lower than encountered previously. However, as small quantities of an absorbing species were still produced, the kinetic technique was altered to use as blank a solution of alkaline aqueous dioxan similar to that used for the ester hydrolysis. This eliminates the effect of absorbance produced in a solvent-alkali reaction.

COMPUTATION OF RESULTS

(a) RATE CONSTANTS BY THE SPECTROPHOTOMETRIC TECHNIQUE

(i) Kinetic Equation

Hydrolysis of the esters studied was carried out in an environment of excess hydroxyl ion. Saponification reactions exhibit kinetics which are overall second order, i.e. first order with respect to both ester and hydroxyl ion concentration.

When hydroxyl ion is present in large excess, the rate of removal of ester is pseudo zero order with respect to hydroxyl ion, and first order with respect to ester concentration, so that the reaction shows pseudo first order kinetics.

$$\text{Rate} = k_2 [\text{Ester}] [OH^-]$$
$$= k_1 [\text{Ester}]$$

where $k_1 = k_2 [OH^-]$ is the pseudo first order rate constant.

The relation assumes that the quantity of hydroxyl ion removed in the reaction

$$RCOOR' + OH^- \longrightarrow RCOO^- + R'OH$$

is neglible compared with the total hydroxyl ion concentration. As was shown previously (see page 57), in the reactions carried out the maximum concentration of hydroxyl ion removed is about

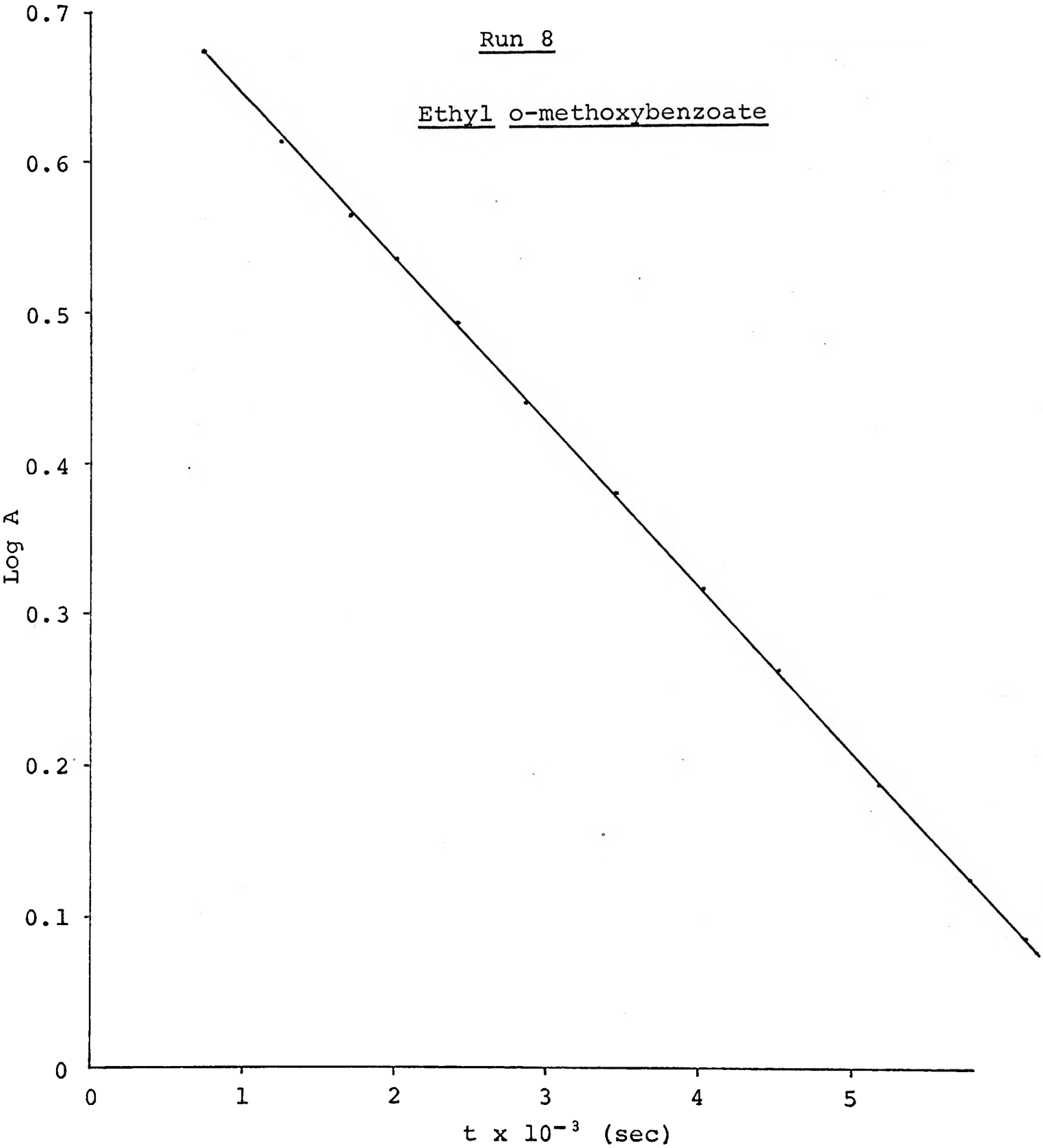


FIGURE 13

First Order Plot.

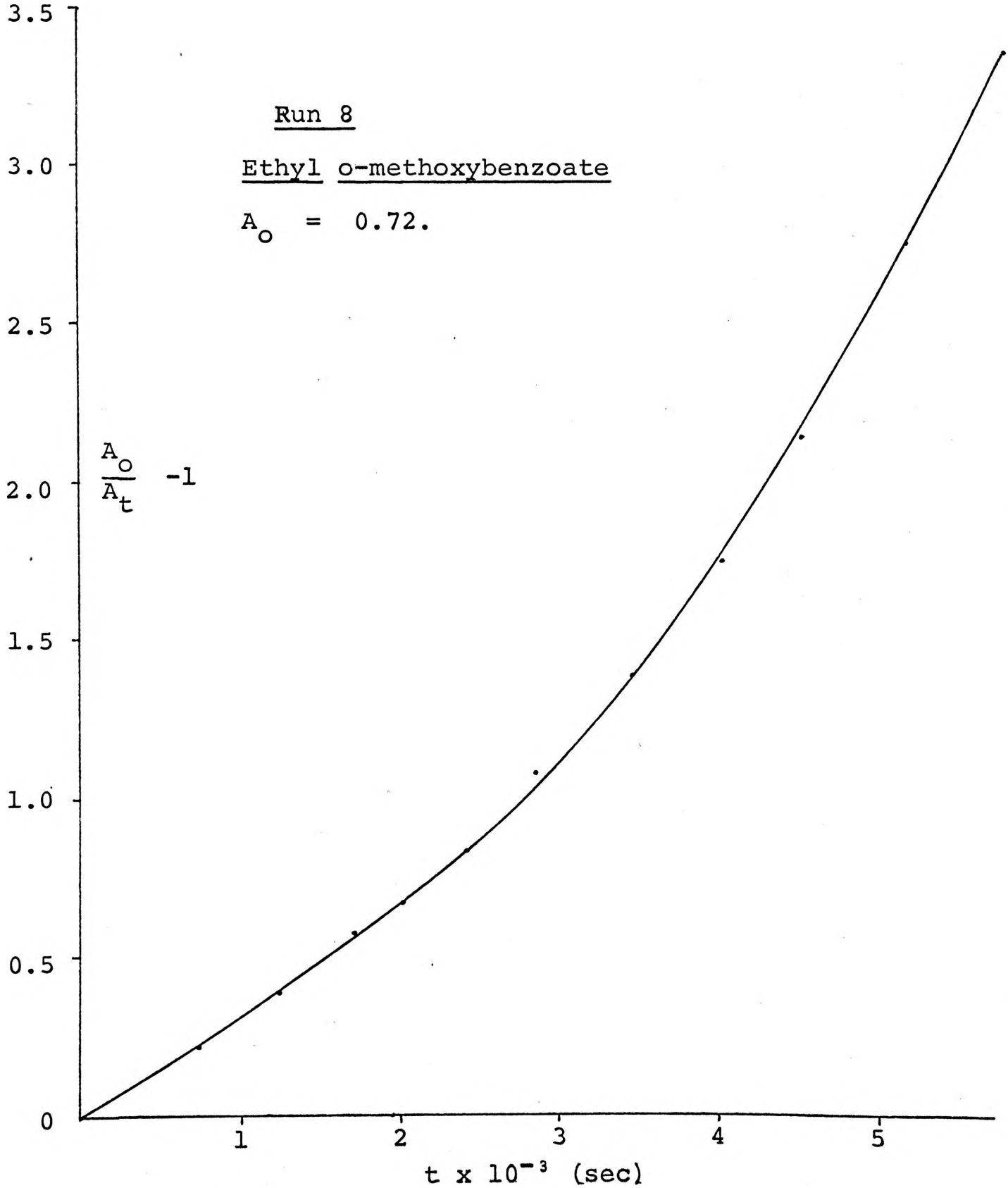


FIGURE 14

Second Order Plot.

1% of the initial concentration, and it is assumed that the use of first order kinetics in calculation of the rate constants is justified.

In Figure 13 a typical set of data are plotted to the first order relationship, and produce a linear plot. Figure 14 illustrates the same set of data plotted to the second order equation, resulting in a curve.

The specific rate constant for the reaction was calculated by dividing the pseudo first order rate constant by the hydroxyl ion concentration

$$k_2 = k_1 / [OH^-]$$

(ii) Calculation of the Rate Constant

From equation (7),

$$c - \ln(A_t - A_\infty) = k_1 t, \qquad \ldots\ldots \qquad (7)$$

k_1 was obtained as the negative slope of the line of best fit plotted through the points $\ln(A_t - A_\infty)$ against t.

The method used for plotting the line of best fit was the method of least squares deviation from the linear regression equation,

$$Y = a + bX, \qquad \ldots\ldots \qquad (22)$$

where $Y = \ln(A_t - A_\infty)$

and $X = t$.

The line of best fit is the line having the

slope [81]

$$b = \frac{\Sigma X \Sigma Y - N\Sigma XY}{(\Sigma X)^2 - N\Sigma X^2} \quad \ldots\ldots \quad (23)$$

and intercept

$$a = \frac{\Sigma XY \Sigma X - N\Sigma XY}{(\Sigma X)^2 - N\Sigma X^2} , \quad \ldots\ldots \quad (24)$$

where N = number of X,Y pairs.

The standard error of estimate of the line of best fit with respect to the data was calculated as

$$S_E = \sqrt{\frac{\Sigma(Y - Y_e)^2}{(N - 1)}} \quad \ldots\ldots \quad (25)$$

where $(Y - Y_e)$ is the difference between a measured value of Y and the value of Y predicted by the line of best fit.

The second order rate constant for the reaction (k_2) was calculated from $k_2 = \frac{-b}{[OH^-]}$, k_2 having the units $l\ mol^{-1}\ sec^{-1}$.

(iii) <u>The Value of A_∞</u>.

Since, in the presence of excess hydroxyl ion the hydrolysis reaction $RCOOR' + OH^- \longrightarrow RCOO^- + R'OH$ will go to completion [82] , A_∞ should, in theory, be zero. However, for the esters studied A_∞ was found to be significantly different from zero, presumably due to absorbance of the anion produced during the reaction. It was not possible to avoid this absorbance because the absorption peak of the anion

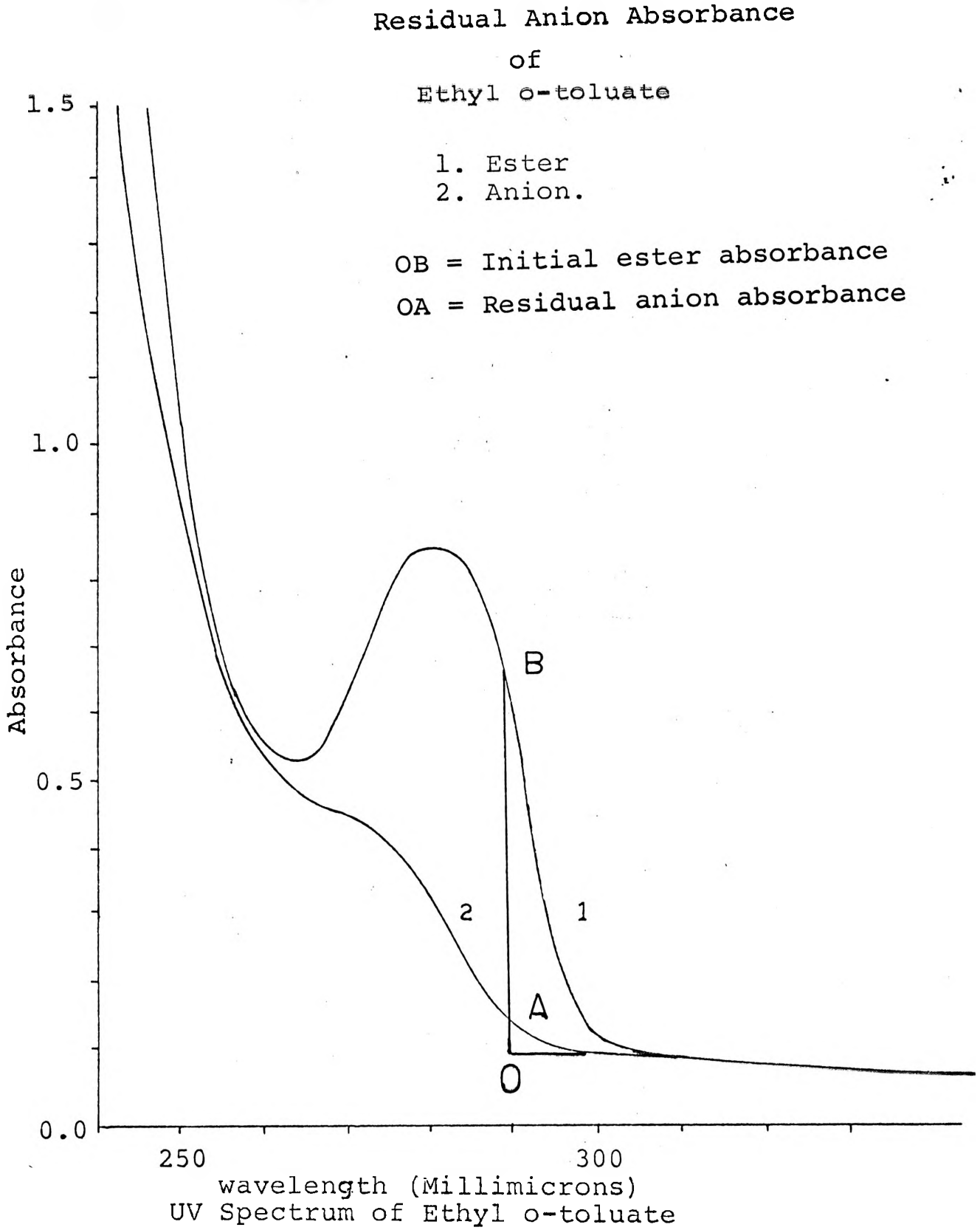

Residual Anion Absorbance
of
Ethyl o-toluate
1. Ester
2. Anion.
OB = Initial ester absorbance
OA = Residual anion absorbance
1.5
1.0
0.5
0.0
Absorbance
B
A
O
1
2
250
300
wavelength (Millimicrons)
UV Spectrum of Ethyl o-toluate

FIGURE 15

partially overlaps that of the ester. This effect was minimised as far as possible by measuring on the "shoulder" of the ester peak. Figure 15 illustrates the residual absorbance of ethyl o-toluate.

The value of A_∞ was found to depend on both the initial ester concentration and the wavelength at which absorption was measured. The values obtained for k were found to be quite sensitive to small variations in A_∞ (see Table 6).

In computing rate constants from the experimental data, A_∞ was assigned an initial value of zero, and the rate constant and standard error of estimate of the line of best fit were calculated from equations (22) - (25). This procedure was then repeated while incrementing A_∞ by 0.010 until the standard error was minimised, and the value of A_∞ was taken as that which best fitted the points to a straight line. The values thus obtained for A_∞ are recorded with the results of each run, and vary from 0.000 to 0.070. It can be seen that the results obtained from similar runs are quite reproducible even though the computed values of A_∞ may differ.

The data in Table 6 illustrate the effect a small variation (0.020) in A_∞ has on the linearity of the plot and the computed rate constant.

TABLE 6

Effect of Variation of A_∞

RUN 4 ETHYL O-METHOXYBENZOATE 44.6 DEG C.

Absorbance	Time	Calc. Absorbance	Difference
.832	510.00	.824	.008
.699	960.00	.694	.005
.580	1440.00	.577	.003
.461	2010.00	.464	-.003
.403	2370.00	.404	-.001
.347	2730.00	.352	-.005
.300	3120.00	.303	-.003
.214	4020.00	.215	-.000
.190	4350.00	.189	.000
.155	4920.00	.152	.003

Least Squares Rate Constant = 0.7274E-02

A_∞ = 0.000

RUN 4 ETHYL O-METHOXYBENZOATE 44.6 DEG C.

Absorbance	Time	Calc. Absorbance	Difference
.832	510.00	.834	-.002
.699	960.00	.698	.001
.580	1440.00	.577	.003
.461	2010.00	.462	-.000
.403	2370.00	.401	.002
.347	2730.00	.349	-.002
.300	3120.00	.301	-.000
.214	4020.00	.214	-.000
.190	4350.00	.190	.000
.155	4920.00	.155	.000

Least Squares Rate Constant = 0.7753E-02

A_∞ = 0.020

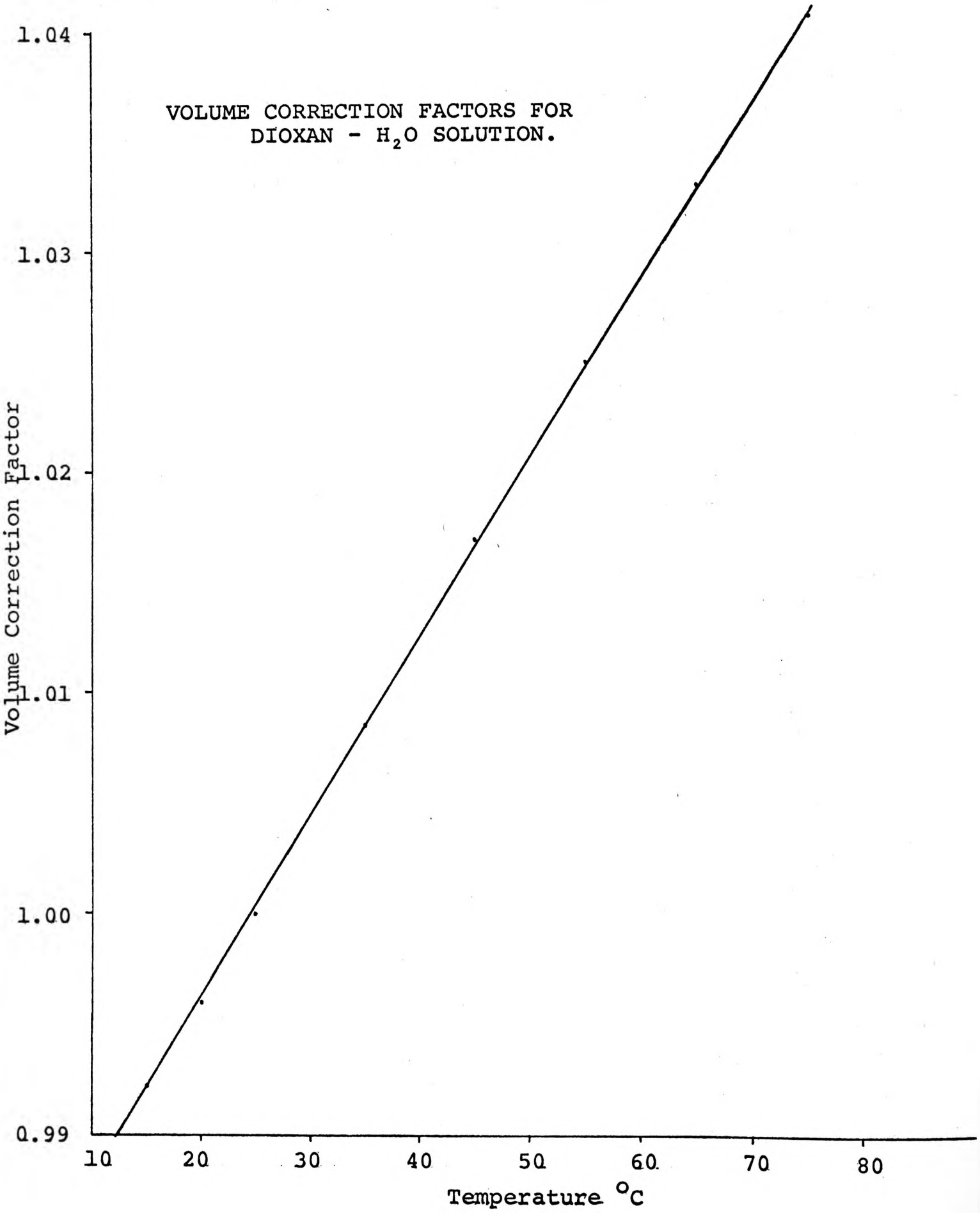

VOLUME CORRECTION FACTORS FOR
DIOXAN - H_2O SOLUTION.
Volume Correction Factor
1.04
1.03
1.02
1.01
1.00
0.99
10
20
30
40
50
60
70
80
Temperature °C

FIGURE 16

(iv) Cell Absorbance

Although "matched" QS quartz cells were used for kinetic runs, their absorbance varied. One of the cells used had a relative absorbance as high as 0.030. Since A_∞ was calculated by the computer as described above, cell absorbance was not recorded as such, but the final absorbance calculated by the computer was cell absorbance plus residual anion absorbance.

(v) Volume Correction Factors

Since solvents expand when heated, the actual concentrations of reacting species are decreased at high temperatures relative to their concentrations at 25°C. The second order rate constant varies inversely with concentration of reactants, and the rate constants obtained must be corrected for solvent expansion by multiplying them by a volume correction factor.

The corrections applied were obtained from the graph shown in Figure 16. These corrections are accurate for solutions which have been standardised at 25°C. They were calculated as ρ_{25}/ρ_t where ρ_{25} is the density of 60% w/v dioxan-water at 25°C., and ρ_t is the solvent density at t°C.

(vi) Computation of Rate Constants

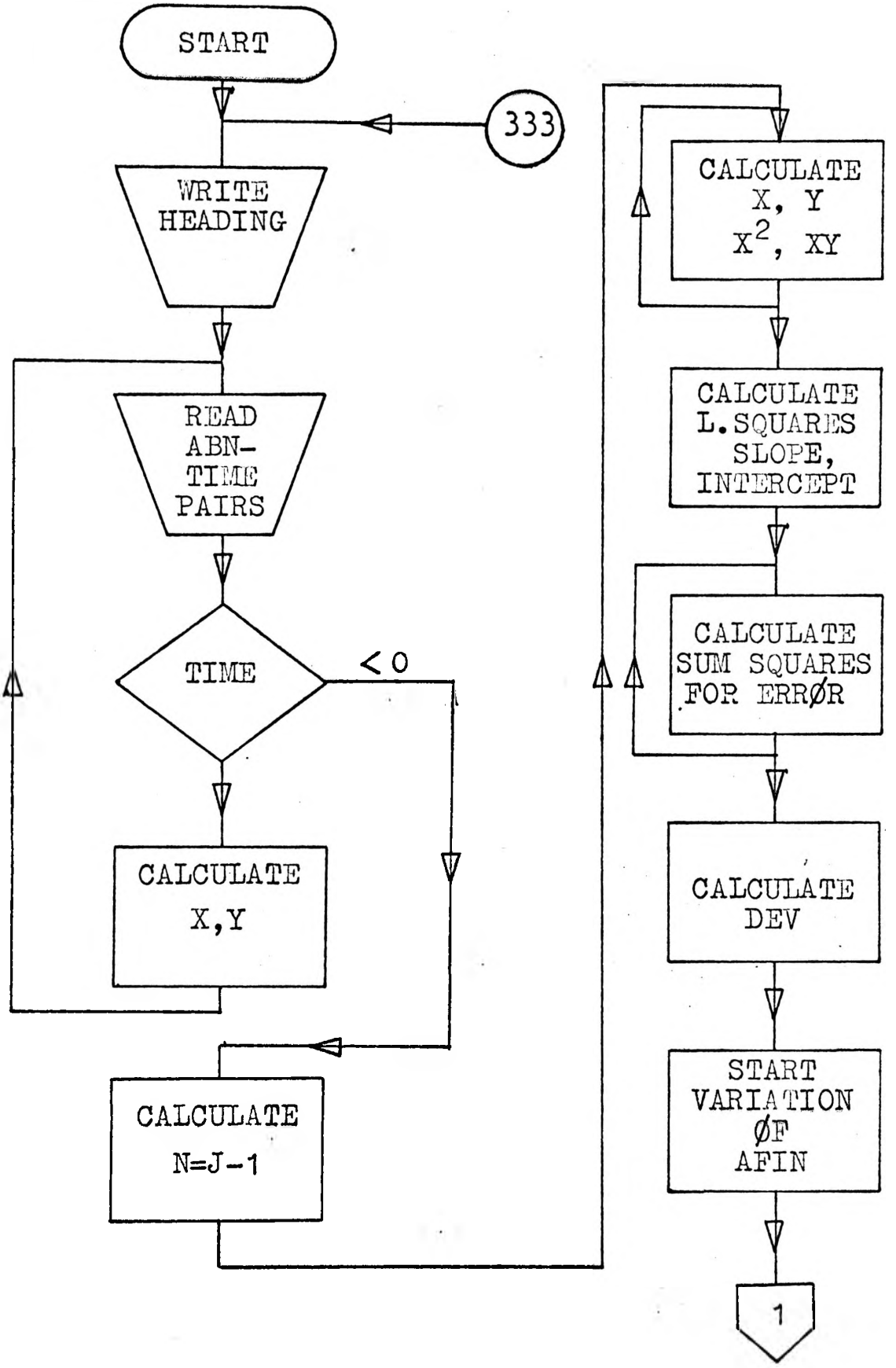
The second order rate constants were computed

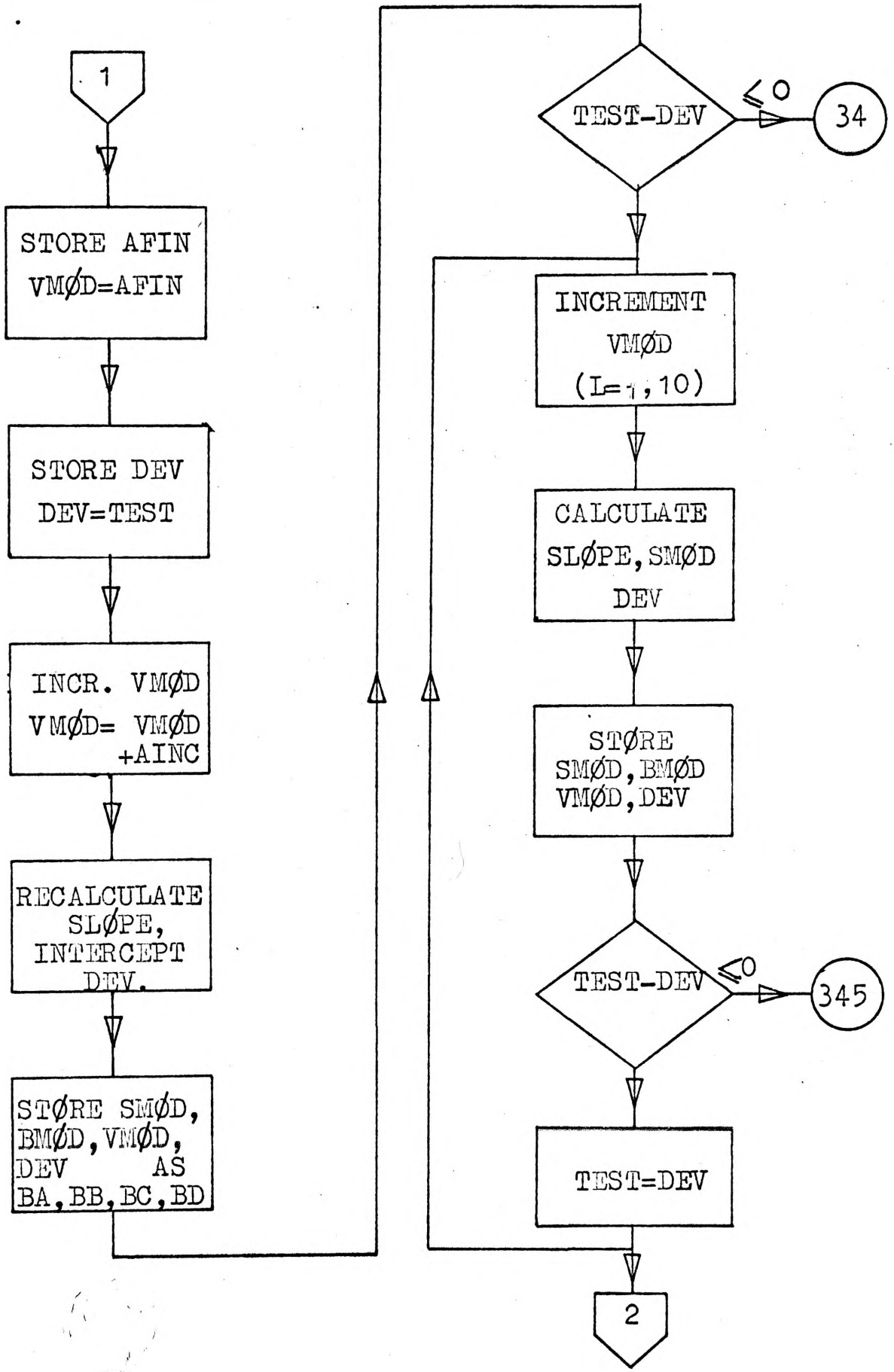
on the IBM 1130 computer at the R.A.N. College, Jervis Bay. The program was written in Fortran IV language [83-85]. Listed below are the variable names used and the flow diagram. The program is listed in the Appendix.

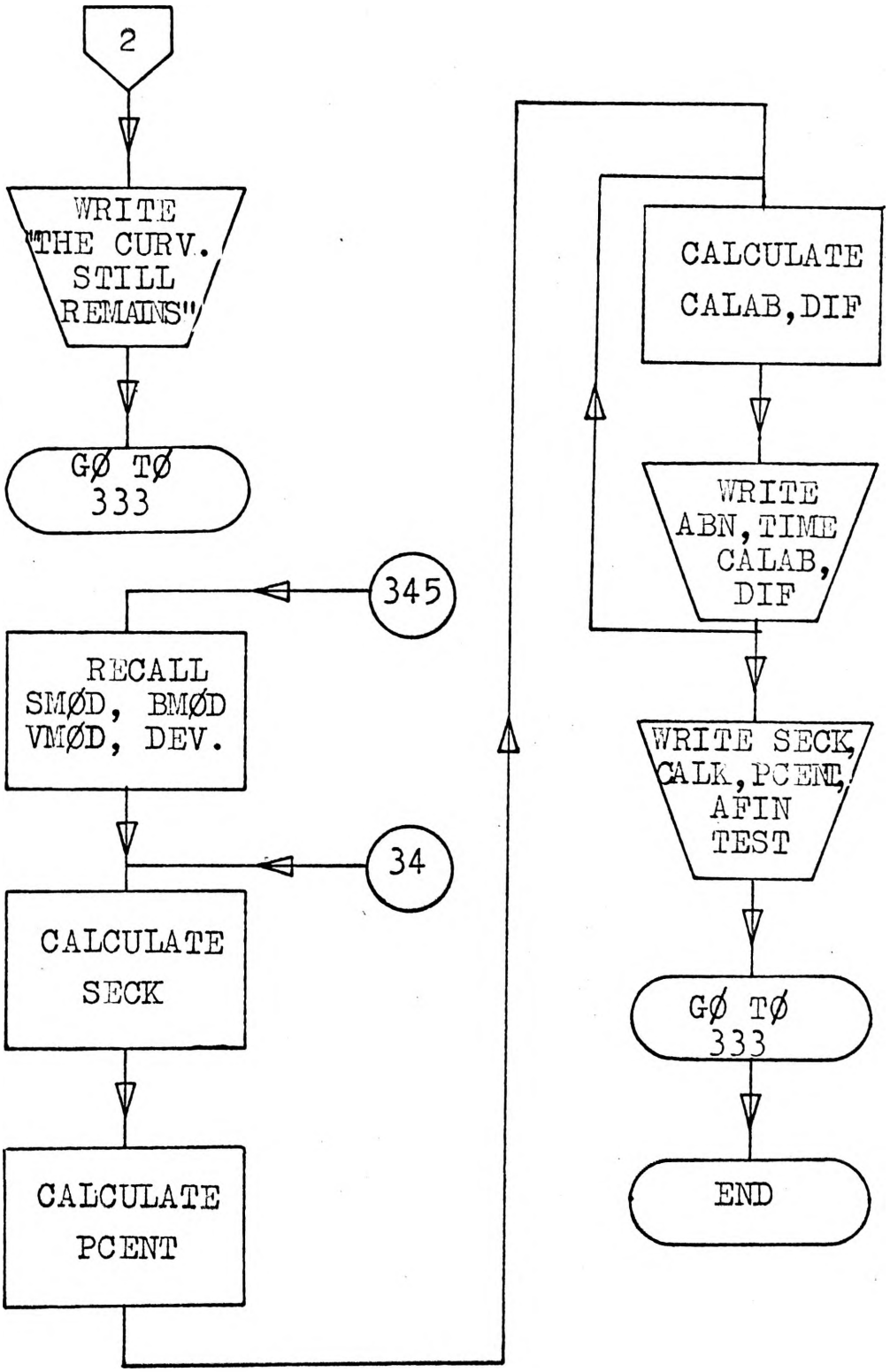
(vii) Program for Calculation of Rate

Constants from Absorbance Data

ABN - absorbance
CALK - alkali concentration
VFAC - volume correction factor
ACELL - cell absorbance
AFIN - absorbance at infinite time
SLØPE - least squares slope
B - intercept of line of best fit
FSUM - sum of squares for error
DEV - standard error of estimate
AINC - increment of AFIN
SMØD - slope obtained with increased AFIN
BMØD - intercept obtained with increased AFIN
RATE - pseudo first order rate constant
SECK - second order rate constant
ABIN - initial absorbance
PCENT - percentage of reaction followed
CALAB - absorbance predicted from least squares slope
DIF - the difference ABN - CALAB


START
333
WRITE HEADING
READ ABN-TIME PAIRS
TIME
< 0
CALCULATE X,Y
CALCULATE N=J-1
CALCULATE X, Y X^2, XY
CALCULATE L. SQUARES SLOPE, INTERCEPT
CALCULATE SUM SQUARES FOR ERRØR
CALCULATE DEV
START VARIATION ØF AFIN
1


1
STORE AFIN
VMØD=AFIN
STORE DEV
DEV=TEST
INCR. VMØD
VMØD= VMØD
+AINC
RECALCULATE
SLØPE,
INTERCEPT
DEV.
STØRE SMØD,
BMØD, VMØD,
DEV AS
BA, BB, BC, BD
TEST-DEV
≤0
34
INCREMENT
VMØD
(L=1,10)
CALCULATE
SLØPE, SMØD
DEV
STØRE
SMØD, BMØD
VMØD, DEV
TEST-DEV
≤0
345
TEST=DEV
2


2
WRITE "THE CURV. STILL REMAINS"
GØ TØ 333
345
RECALL SMØD, BMØD VMØD, DEV.
34
CALCULATE SECK
CALCULATE PCENT
CALCULATE CALAB, DIF
WRITE ABN, TIME CALAB, DIF
WRITE SECK, CALK, PCENT, AFIN TEST
GØ TØ 333
END

(b) RATE CONSTANTS BY THE TITRATION TECHNIQUE

(i) Calculation of the Rate Constant

The rate constant was calculated from equation (1) (page 3),

$$\frac{x}{a(a-x)} = kt \quad . \qquad \ldots\ldots \quad (1)$$

The calculations were carried out on the IBM 1620 computer at the Wollongong University College. Rate constants were calculated for each time-titration pair to check on curvature in the kinetic plot, and the least squares rate constant for each run was calculated from the slope of the line of best fit, as described in section (a).

The program used is described below with a flow diagram, and listed in the Appendix. It is written in Forgo language, and is an adaptation of a program belonging to the computer program library of the Department of Chemistry, Wollongong University College.

(ii) Program for Calculation of Rate Constants from Titration Data

AØ	-	initial concentration of one reactant
BØ	-	initial concentration of other reactant
TNØRM	-	molarity of titrant (NaOH)
ALIQ	-	aliquot of each reaction sample
EACID	-	number of millimoles of hydrochloric acid used to quench the reaction sample

VFAC - volume correction factor

IØRD - a fixed point number assigned as

1 if AØ = BØ
2 " AØ = BØ
3 " AØ = BØ

TITN - volume of titrant

RK - rate constant calculated for each time titration pair

SRSQ - Sum of $(RK)^2$

SUM - Sum of RK

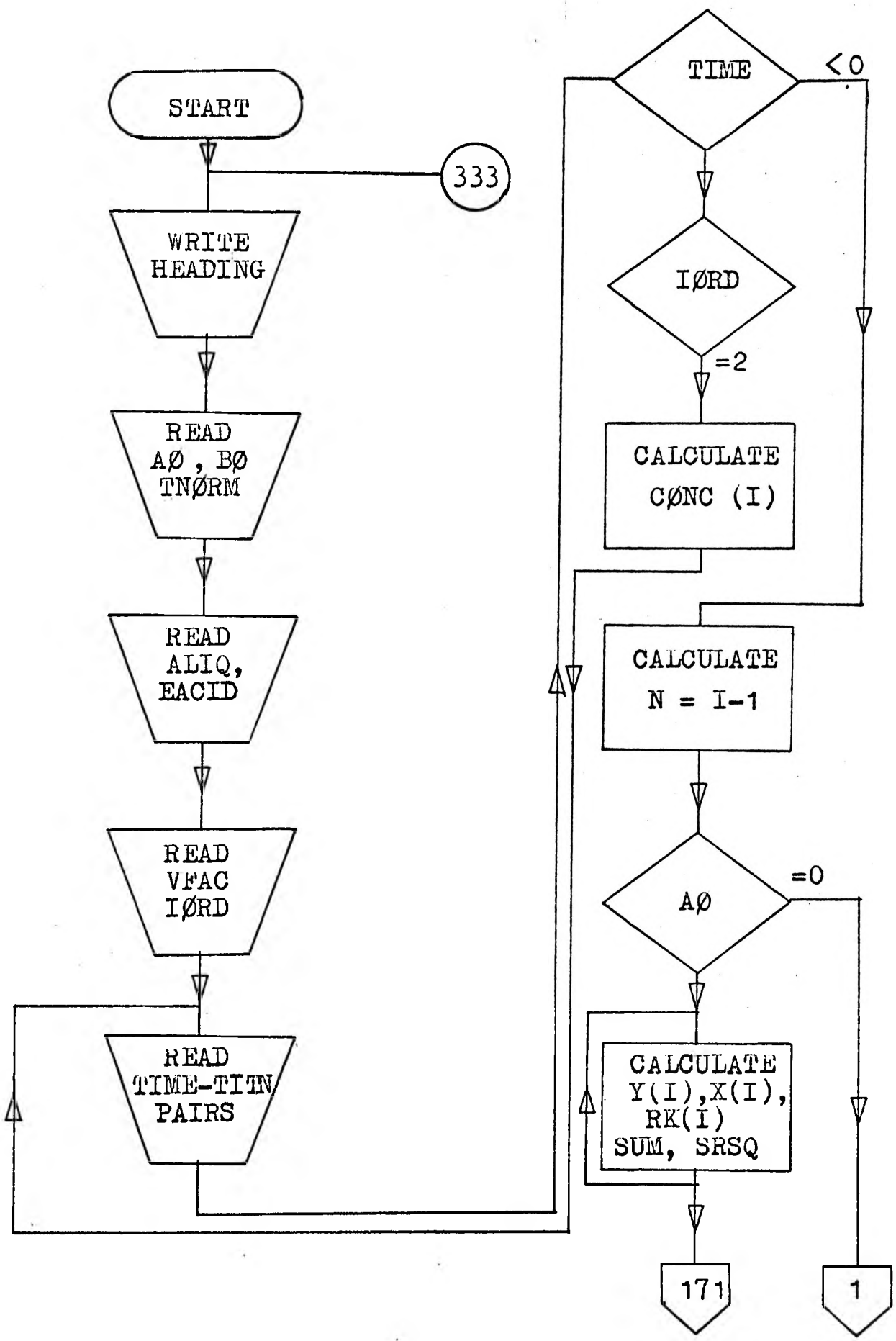
S - slope of line of best fit

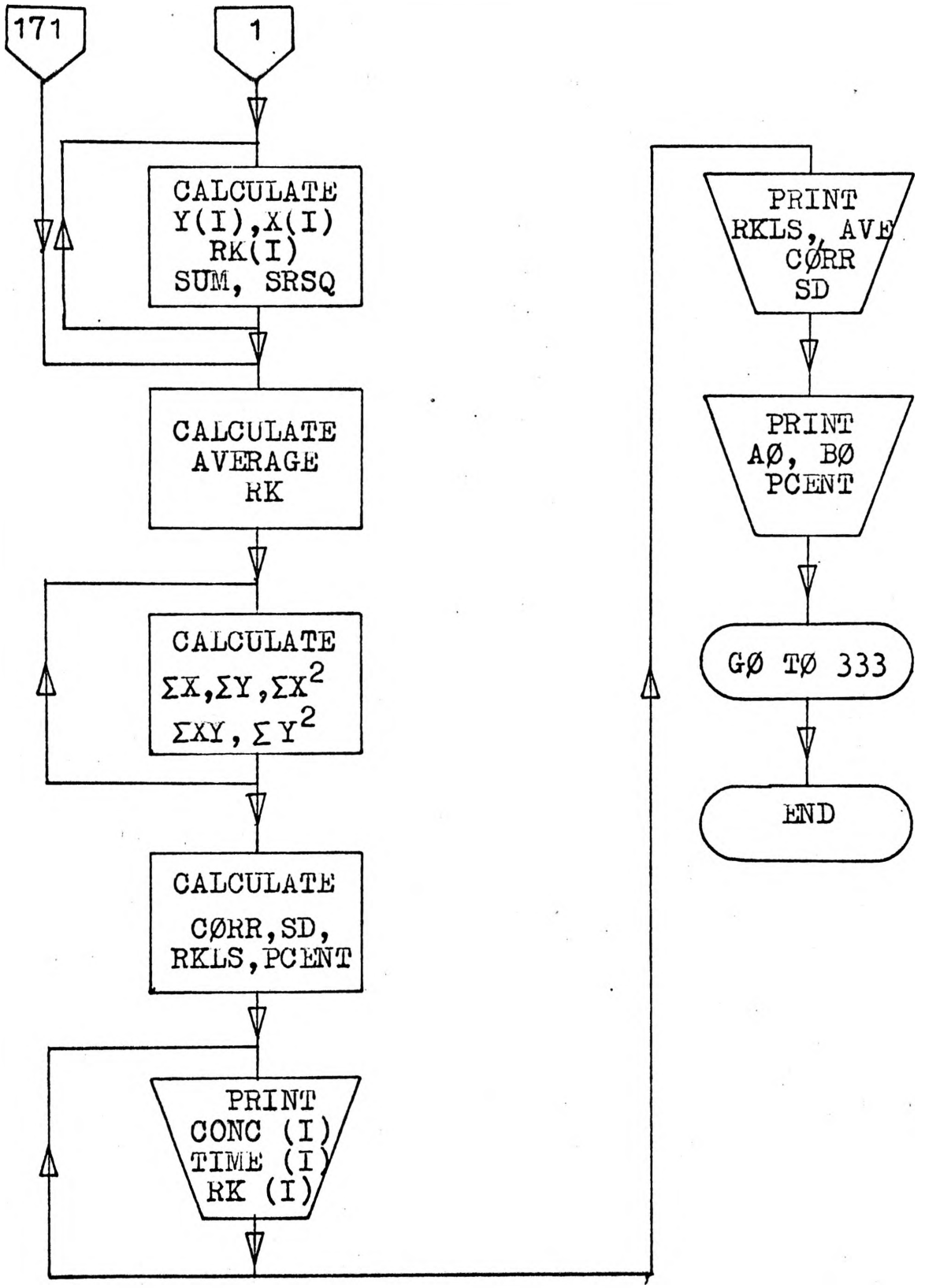
C - intercept of line of best fit

CØRR - correlation coefficient of concentration time pairs

SD - standard deviation of RK values about their mean

RKLS - least squares rate constant


START
333
WRITE HEADING
READ AØ , BØ TNØRM
READ ALIQ, EACID
READ VFAC IØRD
READ TIME-TITN PAIRS
TIME
<0
IØRD
=2
CALCULATE CØNC (I)
CALCULATE N = I-1
AØ
=0
CALCULATE Y(I),X(I), RK(I) SUM, SRSQ
171
1


171
1
CALCULATE
Y(I),X(I)
RK(I)
SUM, SRSQ
CALCULATE
AVERAGE
RK
CALCULATE
ΣX,ΣY,ΣX²
ΣXY, ΣY²
CALCULATE
CØRR,SD,
RKLS,PCENT
PRINT
CONC (I)
TIME (I)
RK (I)
PRINT
RKLS, AVE
CØRR
SD
PRINT
AØ, BØ
PCENT
GØ TØ 333
END

(c) CALCULATION OF AVERAGE RATE CONSTANTS AND THERMODYNAMIC PARAMETERS

(i) Calculation of Thermodynamic Parameters

From equation (15) on page 9,

$$K = \frac{k_B T}{h} e^{\Delta S^*/R} e^{-\Delta H^*/RT} , \quad \ldots\ldots \quad (15)$$

$$\ln \frac{k}{T} = \ln \frac{k_B}{h} + \frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT} . \quad \ldots\ldots \quad (26)$$

The least squares slope was calculated for the plot $\ln k/T$ against $1/T$ for each compound. ΔH^* was calculated from the slope as

$$\Delta H^* = -R \ (\text{slope}).$$

The intercept of the least squares line on the y-axis

$$= \ln \frac{k_B}{h} + \frac{\Delta S^*}{R} ,$$

and ΔS^* was calculated from this relationship. ΔG^* was calculated from ΔH^* and ΔS^* for $T = 318.1^{\circ}K$.

(ii) Calculation of Average Rate Constants

For each compound a number of rate constants were measured experimentally. Because of the nature of the experimental conditions it was not possible to duplicate temperatures exactly (see page 58). The least squares slope of the ART plot was used to calculate average rate constants

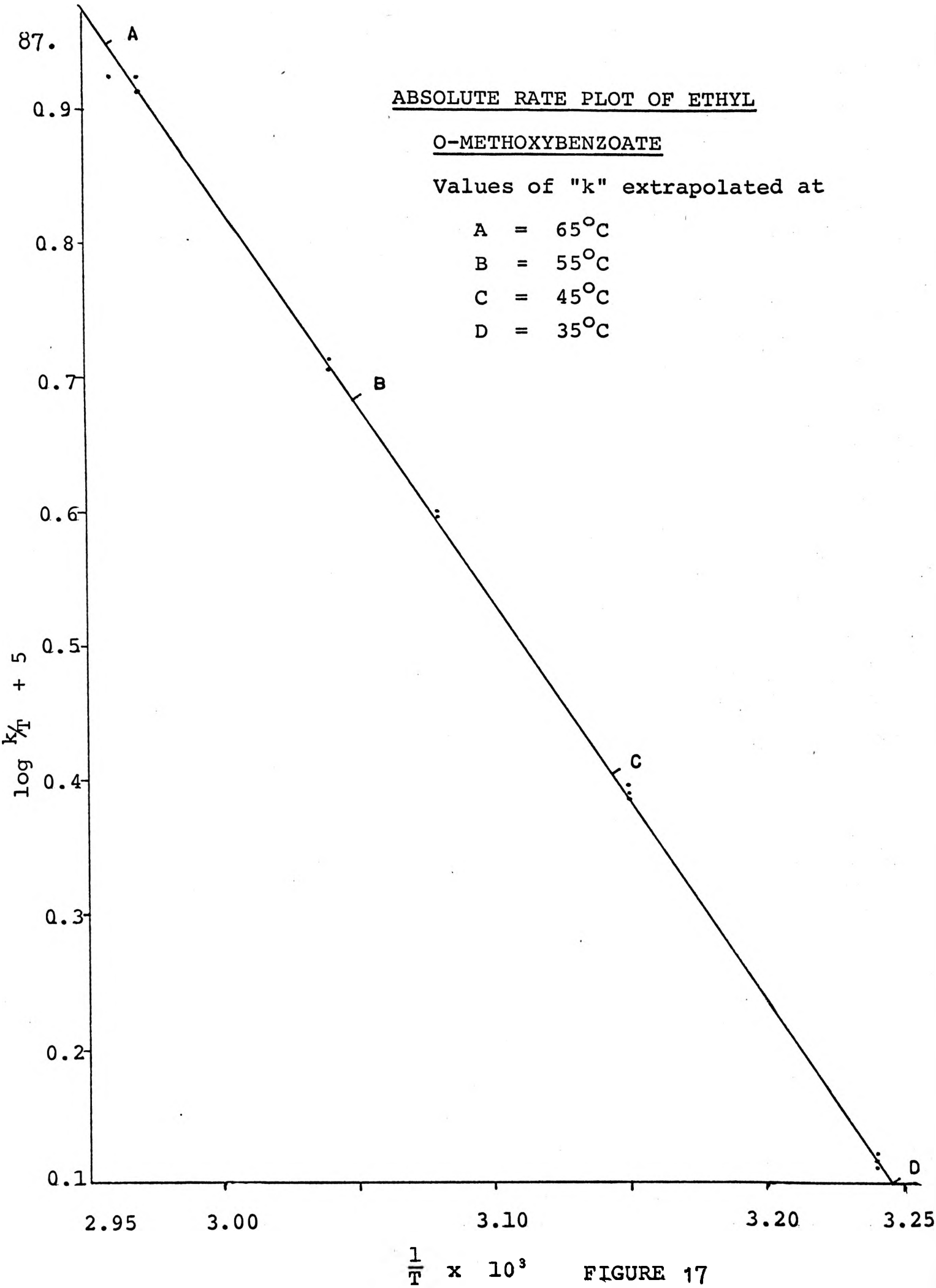

ABSOLUTE RATE PLOT OF ETHYL
O-METHOXYBENZOATE
Values of "k" extrapolated at
A = 65°C
B = 55°C
C = 45°C
D = 35°C
A
B
C
D
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
log k/T + 5
2.95
3.00
3.10
3.20
3.25
1/T x 10³

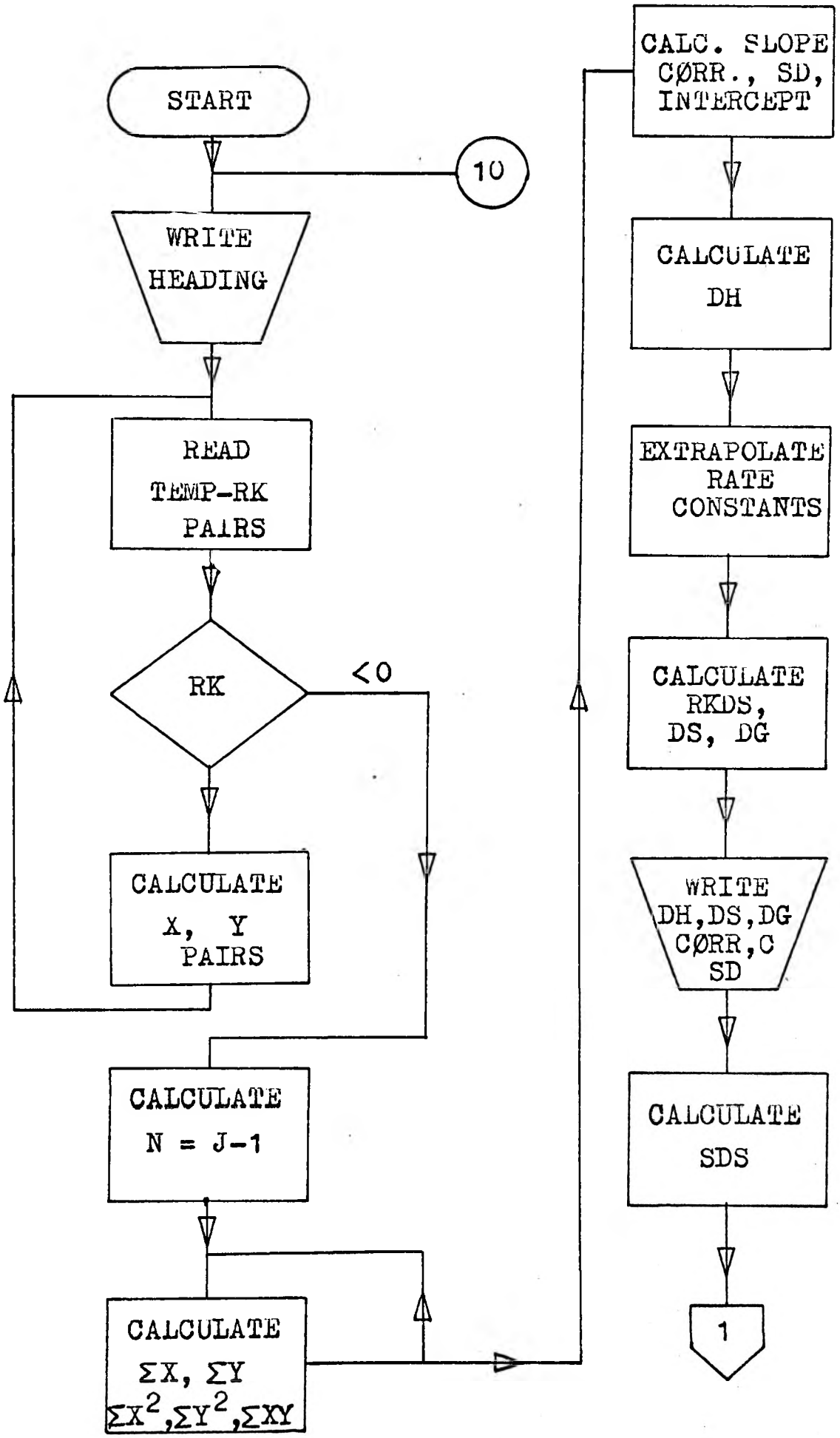
FIGURE 17

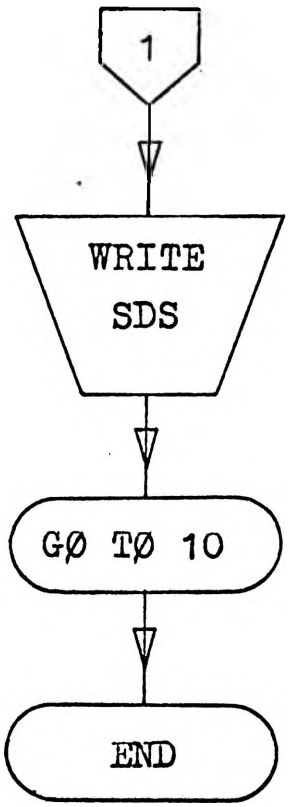
at four temperatures for each compound (see Fig. 17).

(iii) Program for Calculation of Average Rate Constants and Thermodynamic Parameters

The program used was adapted from a program belonging to the computer program library of the Department of Chemistry, Wollongong University College. It is written in Fortran IV, and is described with a flow diagram below and listed in the Appendix.

RK	-	rate constant
S	-	least squares slope
CØRR	-	correlation coefficient of ln $^{k}/_{T}$, $^{1}/_{T}$ pairs
C	-	intercept on Y axis
DH	-	ΔH^{*}
TDS	-	temperature at which ΔG^{*} is calculated
DG	-	ΔG^{*}


START
10
WRITE HEADING
READ TEMP-RK PAIRS
RK
<0
CALCULATE X, Y PAIRS
CALCULATE N = J-1
CALCULATE ΣX, ΣY ΣX², ΣY², ΣXY
CALC. SLOPE CØRR., SD, INTERCEPT
CALCULATE DH
EXTRAPOLATE RATE CONSTANTS
CALCULATE RKDS, DS, DG
WRITE DH,DS,DG CØRR,C SD
CALCULATE SDS
1


1
WRITE
SDS
GØ TØ 10
END

R E S U L T S

The results of the individual kinetic runs for the four esters studied are listed on pages 92-116. The rate constants measured are summarised in Tables 7-11, on pages 117-118. The average extrapolated rate constants and thermodynamic activation parameters are listed in Tables 12 and 13 on page 119.

(a) KINETIC RUNS

RUN 1 ETHYL O-TOLUATE 36.2 DEG C.

ABSORBANCE	TIME	CALC ABSORBANCE	DIFFERENCE
0.702	900.00	0.704	-0.002
0.598	2040.00	0.592	0.005
0.546	2580.00	0.546	-0.000
0.473	3570.00	0.472	0.000
0.439	4080.00	0.438	0.000
0.384	5010.00	0.383	0.000
0.334	5970.00	0.335	-0.001
0.296	6840.00	0.298	-0.002
0.267	7680.00	0.266	0.000
0.238	8580.00	0.237	0.000
0.209	9630.00	0.209	-0.000
0.191	10410.00	0.190	0.000
0.178	11070.00	0.177	0.000

LEAST SQUARES RATE CONSTANT = 0.1082E-02
CATALYST CONCENTRATION =0.15630N
PERCENTAGE OF REACTION FOLLOWED = 84.26
FINAL ABSORBANCE =0.059
STANDARD ERROR OF ESTIMATE =0.00478

RUN 2 ETHYL O-TOLUATE 36.1 DEG C.

ABSORBANCE	TIME	CALC ABSORBANCE	DIFFERENCE
0.553	2070.00	0.555	-0.002
0.512	2610.00	0.511	0.000
0.442	3600.00	0.441	0.000
0.411	4080.00	0.411	-0.000
0.359	5040.00	0.358	0.000
0.314	6000.00	0.313	0.000
0.279	6870.00	0.278	0.000
0.250	7710.00	0.250	-0.000
0.225	8610.00	0.223	0.001
0.197	9660.00	0.197	-0.000
0.180	10440.00	0.181	-0.001
0.170	11100.00	0.169	0.000

LEAST SQUARES RATE CONSTANT = 0.1136E-02
CATALYST CONCENTRATION =0.15630N
PERCENTAGE OF REACTION FOLLOWED = 85.70
FINAL ABSORBANCE =0.069
STANDARD ERROR OF ESTIMATE =0.00571

RUN 3 ETHYL O-TOLUATE 35.1DEG C.

ABSORBANCE	TIME	CALC ABSORBANCE	DIFFERENCE
0.706	1350.00	0.705	0.000
0.652	1740.00	0.653	-0.001
0.570	2460.00	0.568	0.001
0.506	3060.00	0.507	-0.001
0.468	3540.00	0.463	0.004
0.401	4290.00	0.403	-0.002
0.359	4920.00	0.359	-0.000
0.315	5670.00	0.314	0.000
0.289	6120.00	0.290	-0.001
0.254	6870.00	0.255	-0.001
0.238	7320.00	0.236	0.001
0.221	7740.00	0.220	0.000

LEAST SQUARES RATE CONSTANT = 0.1023E-02
CATALYST CONCENTRATION =0.20730N
PERCENTAGE OF REACTION FOLLOWED = 80.36
FINAL ABSORBANCE =0.049
STANDARD ERROR OF ESTIMATE =0.00503

RUN 4 ETHYL O-TOLUATE 44.4 DEG C.

ABSORBANCE	TIME	CALC ABSORBANCE	DIFFERENCE
0.715	660.00	0.719	-0.004
0.640	1020.00	0.630	0.009
0.474	1800.00	0.474	-0.000
0.415	2160.00	0.416	-0.001
0.371	2460.00	0.374	-0.003
0.304	3060.00	0.304	-0.000
0.280	3330.00	0.277	0.002
0.248	3660.00	0.248	-0.000
0.219	4050.00	0.219	-0.000
0.199	4350.00	0.199	-0.000
0.182	4650.00	0.181	0.000

LEAST SQUARES RATE CONSTANT = 0.1929E-02
CATALYST CONCENTRATION =0.20730N
PERCENTAGE OF REACTION FOLLOWED = 83.89
FINAL ABSORBANCE =0.039
STANDARD ERROR OF ESTIMATE =0.00742

RUN 5 ETHYL O-TOLUATE 44.5 DEG C.

ABSORBANCE	TIME	CALC ABSORBANCE	DIFFERENCE
0.687	690.00	0.689	-0.002
0.607	1020.00	0.607	-0.000
0.515	1470.00	0.511	0.003
0.446	1830.00	0.445	0.000
0.346	2490.00	0.348	-0.002
0.283	3090.00	0.279	0.003
0.256	3330.00	0.256	-0.000
0.226	3690.00	0.225	0.000
0.196	4080.00	0.197	-0.001
0.178	4380.00	0.178	-0.000
0.162	4680.00	0.161	0.000

LEAST SQUARES RATE CONSTANT = 0.1983E-02
CATALYST CONCENTRATION =0.20730N
PERCENTAGE OF REACTION FOLLOWED = 84.86
FINAL ABSORBANCE =0.030
STANDARD ERROR OF ESTIMATE =0.00609

RUN 6 ETHYL O-TOLUATE 44.4 DEG C.

ABSORBANCE	TIME	CALC ABSORBANCE	DIFFERENCE
0.698	720.00	0.700	-0.002
0.618	1050.00	0.618	-0.000
0.527	1470.00	0.528	-0.001
0.459	1860.00	0.456	0.002
0.406	2190.00	0.404	0.001
0.358	2520.00	0.358	-0.000
0.292	3120.00	0.289	0.002
0.266	3360.00	0.265	0.000
0.235	3690.00	0.236	-0.001
0.205	4110.00	0.205	-0.000
0.185	4410.00	0.185	-0.000
0.169	4710.00	0.168	0.000

LEAST SQUARES RATE CONSTANT = 0.1939E-02
CATALYST CONCENTRATION =0.20730N
PERCENTAGE OF REACTION FOLLOWED = 84.40
FINAL ABSORBANCE =0.030
STANDARD ERROR OF ESTIMATE =0.00505

RUN 7 ETHYL O-TOLUATE 54.6 DEG C.

ABSORBANCE	TIME	CALC ABSORBANCE	DIFFERENCE
0.478	1890.00	0.477	0.000
0.432	2190.00	0.429	0.002
0.401	2400.00	0.398	0.002
0.365	2640.00	0.366	-0.001
0.328	2940.00	0.330	-0.002
0.292	3360.00	0.286	0.005
0.256	3660.00	0.259	-0.003
0.229	3990.00	0.232	-0.003
0.205	4350.00	0.206	-0.001
0.192	4620.00	0.189	0.002
0.172	4860.00	0.175	-0.003
0.163	5160.00	0.159	0.003

LEAST SQUARES RATE CONSTANT = 0.4089E-02
CATALYST CONCENTRATION =0.09480N
PERCENTAGE OF REACTION FOLLOWED = 85.45
FINAL ABSORBANCE =0.030
STANDARD ERROR OF ESTIMATE =0.01460

RUN 8 ETHYL O-TOLUATE 55.1 DEG C.

ABSORBANCE	TIME	CALC ABSORBANCE	DIFFERENCE
0.426	1560.00	0.423	0.002
0.387	1890.00	0.384	0.002
0.338	2310.00	0.340	-0.002
0.303	2700.00	0.305	-0.002
0.281	3030.00	0.279	0.001
0.252	3390.00	0.253	-0.001
0.214	3990.00	0.217	-0.003
0.189	4620.00	0.186	0.002
0.158	5430.00	0.155	0.002
0.141	5970.00	0.139	0.001
0.118	6810.00	0.119	-0.001
0.110	7320.00	0.109	0.000

LEAST SQUARES RATE CONSTANT = 0.4317E-02
CATALYST CONCENTRATION =0.08180N
PERCENTAGE OF REACTION FOLLOWED = 91.96
FINAL ABSORBANCE =0.059
STANDARD ERROR OF ESTIMATE =0.01521

RUN 9 ETHYL O-TOLUATE 55.2 DEG C.

ABSORBANCE	TIME	CALC ABSORBANCE	DIFFERENCE
0.452	1590.00	0.451	0.000
0.360	2340.00	0.359	0.000
0.314	2760.00	0.317	-0.003
0.288	3090.00	0.288	-0.000
0.263	3450.00	0.260	0.002
0.212	4194.00	0.211	0.000
0.188	4620.00	0.188	-0.000
0.152	5490.00	0.151	0.000
0.132	6060.00	0.131	0.000
0.110	6840.00	0.110	-0.000
0.099	7380.00	0.098	0.000

LEAST SQUARES RATE CONSTANT = 0.4205E-02
CATALYST CONCENTRATION =0.08180N
PERCENTAGE OF REACTION FOLLOWED = 91.58
FINAL ABSORBANCE =0.039
STANDARD ERROR OF ESTIMATE =0.00689

RUN 10 ETHYL O-TOLUATE 64.8 DEG C.

ABSORBANCE	TIME	CALC ABSORBANCE	DIFFERENCE
0.383	870.00	0.380	0.002
0.345	1140.00	0.344	0.000
0.318	1380.00	0.316	0.001
0.281	1680.00	0.286	-0.005
0.260	1980.00	0.259	0.000
0.230	2370.00	0.228	0.001
0.205	2730.00	0.205	-0.000
0.187	3030.00	0.188	-0.001
0.174	3360.00	0.172	0.001
0.158	3660.00	0.159	-0.001
0.149	3960.00	0.148	0.000

LEAST SQUARES RATE CONSTANT = 0.8432E-02
CATALYST CONCENTRATION =0.05460N
PERCENTAGE OF REACTION FOLLOWED = 82.70
FINAL ABSORBANCE =0.069
STANDARD ERROR OF ESTIMATE =0.01187

RUN 11 ETHYL O-TOLUATE 63.6 DEG C.

ABSORBANCE	TIME	CALC ABSORBANCE	DIFFERENCE
0.508	1020.00	0.513	-0.005
0.454	1380.00	0.455	-0.001
0.394	1830.00	0.391	0.002
0.343	2190.00	0.346	-0.003
0.305	2550.00	0.307	-0.002
0.275	2910.00	0.272	0.002
0.242	3300.00	0.239	0.002
0.212	3690.00	0.209	0.002
0.185	4080.00	0.184	0.000
0.163	4470.00	0.161	0.001
0.127	5250.00	0.124	0.002
0.106	5610.00	0.110	-0.004

LEAST SQUARES RATE CONSTANT = 0.7754E-02
CATALYST CONCENTRATION =0.04460N
PERCENTAGE OF REACTION FOLLOWED = 85.33
FINAL ABSORBANCE =0.000
STANDARD ERROR OF ESTIMATE =0.01518

RUN 12 ETHYL O-TOLUATE 65.5 DEG C.

ABSORBANCE	TIME	CALC ABSORBANCE	DIFFERENCE
0.719	870.00	0.717	0.001
0.613	1530.00	0.609	0.003
0.548	1950.00	0.550	-0.002
0.492	2400.00	0.493	-0.001
0.434	2910.00	0.436	-0.002
0.389	3390.00	0.389	-0.000
0.352	3870.00	0.348	0.003
0.316	4320.00	0.313	0.002
0.246	5310.00	0.251	-0.005
0.224	5850.00	0.223	0.000
0.202	6390.00	0.198	0.003
0.180	6840.00	0.181	-0.001

LEAST SQUARES RATE CONSTANT = 0.8592E-02
CATALYST CONCENTRATION =0.03160N
PERCENTAGE OF REACTION FOLLOWED = 83.56
FINAL ABSORBANCE =0.039
STANDARD ERROR OF ESTIMATE =0.01072

RUN 13 ETHYL O-TOLUATE 65.3 DEG C.

ABSORBANCE	TIME	CALC ABSORBANCE	DIFFERENCE
0.680	900.00	0.677	0.002
0.575	1560.00	0.577	-0.002
0.524	1950.00	0.526	-0.002
0.470	2430.00	0.469	0.000
0.420	2940.00	0.417	0.002
0.375	3390.00	0.376	-0.001
0.335	3900.00	0.335	-0.000
0.308	4350.00	0.303	0.004
0.240	5400.00	0.242	-0.002
0.213	5940.00	0.216	-0.003
0.198	6450.00	0.195	0.002
0.181	6870.00	0.180	0.000

LEAST SQUARES RATE CONSTANT = 0.8604E-02
CATALYST CONCENTRATION =0.03160N
PERCENTAGE OF REACTION FOLLOWED = 83.53
FINAL ABSORBANCE =0.049
STANDARD ERROR OF ESTIMATE =0.01061

RUN 1 ETHYL O-CHLOROBENZOATE 27.8 DEG C.

ABSORBANCE	TIME	CALC ABSORBANCE	DIFFERENCE
0.634	600.00	0.633	0.000
0.586	990.00	0.583	0.002
0.537	1380.00	0.537	-0.000
0.494	1770.00	0.494	-0.000
0.446	2280.00	0.445	0.000
0.402	2760.00	0.403	-0.001
0.356	3360.00	0.357	-0.001
0.322	3900.00	0.321	0.000
0.284	4530.00	0.284	-0.000
0.258	5070.00	0.256	0.001
0.233	5580.00	0.233	-0.000
0.208	6240.00	0.207	0.000
0.184	6960.00	0.183	0.000
0.166	7560.00	0.166	-0.000

LEAST SQUARES RATE CONSTANT = 0.7357E-02
CATALYST CONCENTRATION =0.03160N
PERCENTAGE OF REACTION FOLLOWED = 82.70
FINAL ABSORBANCE =0.049
STANDARD ERROR OF ESTIMATE =0.00341

RUN 2 ETHYL O-CHLOROBENZOATE 27.8 DEG C.

ABSORBANCE	TIME	CALC ABSORBANCE	DIFFERENCE
0.634	630.00	0.637	-0.003
0.589	1020.00	0.586	0.002
0.540	1410.00	0.539	0.000
0.497	1800.00	0.496	0.000
0.448	2310.00	0.446	0.001
0.403	2820.00	0.401	0.001
0.356	3390.00	0.357	-0.001
0.318	3930.00	0.320	-0.002
0.283	4560.00	0.282	0.000
0.256	5100.00	0.254	0.001
0.230	5610.00	0.231	-0.001
0.205	6270.00	0.204	0.000
0.180	6990.00	0.179	0.000
0.161	7590.00	0.161	-0.000

LEAST SQUARES RATE CONSTANT = 0.7257E-02
CATALYST CONCENTRATION =0.03160N
PERCENTAGE OF REACTION FOLLOWED = 82.45
FINAL ABSORBANCE =0.039
STANDARD ERROR OF ESTIMATE =0.00474

RUN 3 ETHYL O-CHLOROBENZOATE 27.7 DEG C.

ABSORBANCE	TIME	CALC ABSORBANCE	DIFFERENCE
0.587	1590.00	0.586	0.000
0.472	2370.00	0.472	-0.000
0.420	2820.00	0.419	0.000
0.366	3330.00	0.367	-0.001
0.320	3870.00	0.320	-0.000
0.290	4320.00	0.287	0.002
0.260	4710.00	0.262	-0.002
0.238	5160.00	0.237	0.000
0.214	5700.00	0.212	0.001
0.195	6180.00	0.193	0.001
0.175	6690.00	0.175	-0.000
0.163	7110.00	0.163	-0.000

LEAST SQUARES RATE CONSTANT = 0.7334E-02
CATALYST CONCENTRATION =0.04460N
PERCENTAGE OF REACTION FOLLOWED = 90.25
FINAL ABSORBANCE =0.079
STANDARD ERROR OF ESTIMATE =0.00875

RUN 4 ETHYL O-CHLOROBENZOATE 36.2 DEG C.

ABSORBANCE	TIME	CALC ABSORBANCE	DIFFERENCE
0.503	900.00	0.505	-0.002
0.464	1440.00	0.462	0.001
0.423	2040.00	0.420	0.002
0.383	2640.00	0.381	0.001
0.342	3300.00	0.343	-0.001
0.312	3870.00	0.314	-0.002
0.284	4530.00	0.283	0.000
0.250	5310.00	0.251	-0.001
0.226	6030.00	0.225	0.000
0.210	6510.00	0.209	0.000
0.191	7140.00	0.191	-0.000
0.179	7590.00	0.179	-0.000
0.171	7920.00	0.170	0.000

LEAST SQUARES RATE CONSTANT = 0.1198E-01
CATALYST CONCENTRATION =0.01460N
PERCENTAGE OF REACTION FOLLOWED = 74.61
FINAL ABSORBANCE =0.030
STANDARD ERROR OF ESTIMATE =0.00428

RUN 5 ETHYL O-CHLOROBENZOATE 36.2 DEG C.

ABSORBANCE	TIME	CALC ABSORBANCE	DIFFERENCE
0.580	900.00	0.578	0.001
0.530	1470.00	0.529	0.000
0.484	2070.00	0.482	0.001
0.438	2670.00	0.439	-0.001
0.398	3330.00	0.397	0.000
0.364	3900.00	0.365	-0.001
0.330	4560.00	0.331	-0.001
0.294	5340.00	0.295	-0.001
0.268	6060.00	0.266	0.001
0.251	6510.00	0.250	0.000
0.230	7170.00	0.229	0.000
0.216	7620.00	0.215	0.000
0.206	7950.00	0.206	-0.000

LEAST SQUARES RATE CONSTANT = 0.1194E-01
CATALYST CONCENTRATION =0.01460N
PERCENTAGE OF REACTION FOLLOWED = 74.75
FINAL ABSORBANCE =0.049
STANDARD ERROR OF ESTIMATE =0.00372

RUN 6 ETHYL O-CHLOROBENZOATE 35.9 DEG C.

ABSORBANCE	TIME	CALC ABSORBANCE	DIFFERENCE
0.562	360.00	0.558	0.003
0.503	840.00	0.503	-0.000
0.450	1350.00	0.452	-0.002
0.412	1800.00	0.411	0.000
0.374	2250.00	0.375	-0.001
0.338	2760.00	0.339	-0.001
0.310	3210.00	0.310	-0.000
0.280	3750.00	0.280	-0.000
0.256	4260.00	0.255	0.000
0.233	4800.00	0.232	0.000
0.205	5550.00	0.204	0.000
0.189	6090.00	0.187	0.001
0.171	6720.00	0.170	0.000
0.146	7800.00	0.146	-0.000

LEAST SQUARES RATE CONSTANT = 0.1194E-01
CATALYST CONCENTRATION =0.02100N
PERCENTAGE OF REACTION FOLLOWED = 85.77
FINAL ABSORBANCE =0.069
STANDARD ERROR OF ESTIMATE =0.00583

RUN 7 ETHYL O-CHLOROBENZOATE 45.3 DEG C.

ABSORBANCE	TIME	CALC ABSORBANCE	DIFFERENCE
0.508	1080.00	0.509	-0.001
0.454	1500.00	0.452	0.001
0.406	1890.00	0.405	0.000
0.365	2280.00	0.363	0.001
0.330	2640.00	0.329	0.000
0.298	3000.00	0.298	-0.000
0.271	3360.00	0.270	0.000
0.236	3870.00	0.236	-0.000
0.206	4380.00	0.206	-0.000
0.176	4920.00	0.180	-0.004
0.156	5520.00	0.155	0.000
0.137	6090.00	0.135	0.001
0.115	6810.00	0.114	0.000

LEAST SQUARES RATE CONSTANT	= 0.2105E-01
CATALYST CONCENTRATION	=0.01460N
PERCENTAGE OF REACTION FOLLOWED	= 87.20
FINAL ABSORBANCE	=0.030
STANDARD ERROR OF ESTIMATE	=0.00932

RUN 8 ETHYL O-CHLOROBENZOATE 44.7 DEG C.

ABSORBANCE	TIME	CALC ABSORBANCE	DIFFERENCE
0.530	870.00	0.530	-0.000
0.460	1290.00	0.457	0.002
0.413	1590.00	0.412	0.000
0.365	1950.00	0.365	-0.000
0.331	2220.00	0.335	-0.004
0.301	2550.00	0.301	-0.000
0.248	3240.00	0.245	0.002
0.222	3630.00	0.220	0.001
0.202	3960.00	0.202	-0.000
0.185	4320.00	0.185	-0.000
0.169	4740.00	0.168	0.000
0.151	5250.00	0.151	-0.000
0.137	5760.00	0.137	-0.000

LEAST SQUARES RATE CONSTANT	= 0.1992E-01
CATALYST CONCENTRATION	=0.02150N
PERCENTAGE OF REACTION FOLLOWED	= 91.22
FINAL ABSORBANCE	=0.079
STANDARD ERROR OF ESTIMATE	=0.00739

RUN 9 ETHYL O-CHLOROBENZOATE 44.9 DEG C.

ABSORBANCE	TIME	CALC ABSORBANCE	DIFFERENCE
0.492	900.00	0.490	0.001
0.421	1290.00	0.423	-0.002
0.376	1620.00	0.375	0.000
0.332	1950.00	0.333	-0.001
0.300	2250.00	0.300	-0.000
0.270	2580.00	0.268	0.001
0.216	3270.00	0.214	0.001
0.192	3630.00	0.192	-0.000
0.174	3990.00	0.173	0.000
0.158	4320.00	0.158	-0.000
0.141	4770.00	0.140	0.000
0.122	5280.00	0.124	-0.002
0.114	5790.00	0.112	0.001

LEAST SQUARES RATE CONSTANT = 0.2040E-01
CATALYST CONCENTRATION =0.02150N
PERCENTAGE OF REACTION FOLLOWED = 91.48
FINAL ABSORBANCE =0.059
STANDARD ERROR OF ESTIMATE =0.01689

RUN 10 ETHYL O-CHLOROBENZOATE 50.2 DEG C.

ABSORBANCE	TIME	CALC ABSORBANCE	DIFFERENCE
0.617	480.00	0.611	0.005
0.545	900.00	0.547	-0.002
0.483	1380.00	0.484	-0.001
0.438	1770.00	0.439	-0.001
0.392	2250.00	0.392	-0.000
0.353	2700.00	0.354	-0.001
0.320	3150.00	0.321	-0.001
0.291	3660.00	0.289	0.001
0.268	4110.00	0.266	0.001
0.244	4620.00	0.243	0.000
0.227	5040.00	0.227	-0.000
0.207	5640.00	0.207	-0.000

LEAST SQUARES RATE CONSTANT = 0.2584E-01
CATALYST CONCENTRATION =0.01320N
PERCENTAGE OF REACTION FOLLOWED = 75.74
FINAL ABSORBANCE =0.049
STANDARD ERROR OF ESTIMATE =0.00672

RUN 11 ETHYL O-CHLOROBENZOATE 50.3 DEG C.

ABSORBANCE	TIME	CALC ABSORBANCE	DIFFERENCE
0.622	510.00	0.622	-0.000
0.545	930.00	0.548	-0.003
0.477	1410.00	0.476	0.000
0.428	1800.00	0.426	0.001
0.376	2280.00	0.375	0.000
0.334	2730.00	0.334	-0.000
0.301	3180.00	0.300	0.000
0.271	3690.00	0.268	0.002
0.246	4140.00	0.245	0.000
0.221	4650.00	0.222	-0.001
0.206	5070.00	0.207	-0.001
0.189	5730.00	0.188	0.000

LEAST SQUARES RATE CONSTANT = 0.2756E-01
CATALYST CONCENTRATION =0.01420N
PERCENTAGE OF REACTION FOLLOWED = 80.78
FINAL ABSORBANCE =0.059
STANDARD ERROR OF ESTIMATE =0.01035

RUN 12 ETHYL O-CHLOROBENZOATE 53.2 DEG C.

ABSORBANCE	TIME	CALC ABSORBANCE	DIFFERENCE
0.441	870.00	0.440	0.000
0.386	1230.00	0.384	0.001
0.346	1500.00	0.347	-0.001
0.310	1800.00	0.311	-0.001
0.278	2100.00	0.278	-0.000
0.241	2520.00	0.240	0.000
0.219	2790.00	0.218	0.000
0.192	3180.00	0.191	0.000
0.175	3480.00	0.173	0.001
0.157	3780.00	0.157	-0.000

LEAST SQUARES RATE CONSTANT = 0.3257E-01
CATALYST CONCENTRATION =0.01320N
PERCENTAGE OF REACTION FOLLOWED = 79.73
FINAL ABSORBANCE =0.039
STANDARD ERROR OF ESTIMATE =0.00486

RUN 1 ETHYL O-METHOXYBENZOATE 36.0 DEG C.

ABSORBANCE	TIME	CALC ABSORBANCE	DIFFERENCE
0.744	840.00	0.744	-0.000
0.662	1470.00	0.662	-0.000
0.589	2130.00	0.587	0.001
0.532	2670.00	0.533	-0.001
0.477	3300.00	0.476	0.000
0.422	3990.00	0.422	-0.000
0.385	4530.00	0.384	0.000
0.346	5160.00	0.345	0.000
0.315	5700.00	0.315	-0.000
0.261	6900.00	0.259	0.001
0.234	7560.00	0.233	0.000
0.215	8070.00	0.216	-0.001

LEAST SQUARES RATE CONSTANT = 0.3982E-02
CATALYST CONCENTRATION =0.05010N
PERCENTAGE OF REACTION FOLLOWED = 79.86
FINAL ABSORBANCE =0.049
STANDARD ERROR OF ESTIMATE =0.00331

RUN 2 ETHYL O-METHOXYBENZOATE 35.8 DEG C.

ABSORBANCE	TIME	CALC ABSORBANCE	DIFFERENCE
0.800	750.00	0.799	0.000
0.673	1500.00	0.673	-0.000
0.591	2100.00	0.588	0.002
0.519	2670.00	0.518	0.000
0.454	3300.00	0.452	0.001
0.387	4020.00	0.388	-0.001
0.343	4590.00	0.345	-0.002
0.306	5220.00	0.305	0.000
0.259	6120.00	0.257	0.001
0.237	6480.00	0.240	-0.003
0.220	7020.00	0.219	0.000
0.194	7770.00	0.193	0.000
0.169	8640.00	0.168	0.000

LEAST SQUARES RATE CONSTANT = 0.4069E-02
CATALYST CONCENTRATION =0.06280N
PERCENTAGE OF REACTION FOLLOWED = 88.78
FINAL ABSORBANCE =0.069
STANDARD ERROR OF ESTIMATE =0.00828

RUN 3 ETHYL O-METHOXYBENZOATE 35.8 DEG C.

ABSORBANCE	TIME	CALC ABSORBANCE	DIFFERENCE
0.774	810.00	0.776	-0.002
0.647	1560.00	0.649	-0.002
0.564	2160.00	0.564	-0.000
0.498	2730.00	0.494	0.003
0.434	3330.00	0.431	0.002
0.366	4050.00	0.367	-0.001
0.322	4650.00	0.323	-0.001
0.286	5280.00	0.282	0.003
0.237	6150.00	0.237	-0.000
0.216	6540.00	0.219	-0.003
0.202	7050.00	0.199	0.002
0.173	7830.00	0.173	-0.000
0.149	8700.00	0.149	-0.000

LEAST SQUARES RATE CONSTANT = 0.4141E-02
CATALYST CONCENTRATION =0.06280N
PERCENTAGE OF REACTION FOLLOWED = 89.93
FINAL ABSORBANCE =0.059
STANDARD ERROR OF ESTIMATE =0.00962

RUN 4 ETHYL O-METHOXYBENZOATE 44.6 DEG C.

ABSORBANCE	TIME	CALC ABSORBANCE	DIFFERENCE
0.832	510.00	0.834	-0.002
0.699	960.00	0.697	0.001
0.580	1440.00	0.577	0.002
0.461	2010.00	0.461	-0.000
0.403	2370.00	0.401	0.001
0.347	2730.00	0.349	-0.002
0.300	3120.00	0.300	-0.000
0.214	4020.00	0.214	-0.000
0.190	4350.00	0.189	0.000
0.155	4920.00	0.154	0.000

LEAST SQUARES RATE CONSTANT = 0.7753E-02
CATALYST CONCENTRATION =0.05350N
PERCENTAGE OF REACTION FOLLOWED = 86.53
FINAL ABSORBANCE =0.020
STANDARD ERROR OF ESTIMATE =0.00346

RUN 5 ETHYL O-METHOXYBENZOATE 44.5 DEG C.

ABSORBANCE	TIME	CALC ABSORBANCE	DIFFERENCE
0.557	810.00	0.560	-0.003
0.498	1080.00	0.497	0.000
0.442	1380.00	0.436	0.005
0.344	1920.00	0.347	-0.003
0.298	2310.00	0.296	0.001
0.268	2580.00	0.265	0.002
0.232	2910.00	0.233	-0.001
0.187	3450.00	0.191	-0.004
0.173	3780.00	0.170	0.002
0.155	4080.00	0.154	0.000
0.135	4500.00	0.134	0.000
0.120	4890.00	0.120	-0.000

LEAST SQUARES RATE CONSTANT = 0.7863E-02
CATALYST CONCENTRATION =0.06280N
PERCENTAGE OF REACTION FOLLOWED = 90.74
FINAL ABSORBANCE =0.049
STANDARD ERROR OF ESTIMATE =0.01337

RUN 6 ETHYL O-METHOXYBENZOATE 44.3 DEG C.

ABSORBANCE	TIME	CALC ABSORBANCE	DIFFERENCE
0.546	840.00	0.548	-0.002
0.486	1110.00	0.486	-0.000
0.428	1410.00	0.425	0.002
0.335	1950.00	0.336	-0.001
0.285	2340.00	0.284	0.000
0.256	2580.00	0.257	-0.001
0.222	2940.00	0.221	0.000
0.180	3480.00	0.178	0.001
0.156	3810.00	0.156	-0.000
0.141	4110.00	0.139	0.001
0.120	4530.00	0.120	-0.000
0.104	4920.00	0.104	-0.000

LEAST SQUARES RATE CONSTANT = 0.7677E-02
CATALYST CONCENTRATION =0.06280N
PERCENTAGE OF REACTION FOLLOWED = 90.42
FINAL ABSORBANCE =0.030
STANDARD ERROR OF ESTIMATE =0.00655

RUN 7 ETHYL O-METHOXYBENZOATE 52.7 DEG C.

ABSORBANCE	TIME	CALC ABSORBANCE	DIFFERENCE
0.897	720.00	0.894	0.002
0.794	1200.00	0.795	-0.001
0.707	1650.00	0.712	-0.005
0.661	1950.00	0.662	-0.001
0.602	2370.00	0.598	0.003
0.537	2850.00	0.533	0.003
0.470	3420.00	0.465	0.004
0.407	3990.00	0.407	-0.000
0.362	4470.00	0.364	-0.002
0.309	5130.00	0.312	-0.003
0.275	5730.00	0.272	0.002
0.248	6150.00	0.248	-0.000

LEAST SQUARES RATE CONSTANT = 0.1344E-01
CATALYST CONCENTRATION =0.01930N
PERCENTAGE OF REACTION FOLLOWED = 78.24
FINAL ABSORBANCE =0.020
STANDARD ERROR OF ESTIMATE =0.00672

RUN 8 ETHYL O-METHOXYBENZOATE 52.8 DEG C.

ABSORBANCE	TIME	CALC ABSORBANCE	DIFFERENCE
0.595	750.00	0.591	0.003
0.520	1260.00	0.521	-0.001
0.462	1710.00	0.466	-0.004
0.434	2010.00	0.432	0.001
0.392	2430.00	0.390	0.001
0.347	2880.00	0.348	-0.001
0.302	3480.00	0.300	0.001
0.262	4020.00	0.261	0.000
0.230	4530.00	0.230	-0.000
0.193	5190.00	0.194	-0.001
0.167	5790.00	0.167	-0.000
0.151	6210.00	0.149	0.001

LEAST SQUARES RATE CONSTANT = 0.1286E-01
CATALYST CONCENTRATION =0.01930N
PERCENTAGE OF REACTION FOLLOWED = 78.76
FINAL ABSORBANCE =0.000
STANDARD ERROR OF ESTIMATE =0.00536

RUN 9 ETHYL O-METHOXYBENZOATE 55.2 DEG C.

ABSORBANCE	TIME	CALC ABSORBANCE	DIFFERENCE
0.603	390.00	0.608	-0.005
0.527	840.00	0.523	0.003
0.459	1230.00	0.460	-0.001
0.408	1620.00	0.406	0.001
0.357	2040.00	0.354	0.002
0.310	2460.00	0.310	-0.000
0.270	2970.00	0.265	0.004
0.230	3450.00	0.230	-0.000
0.197	3930.00	0.200	-0.003
0.176	4350.00	0.177	-0.001
0.156	4860.00	0.154	0.001
0.136	5370.00	0.135	0.000

LEAST SQUARES RATE CONSTANT = 0.1690E-01
CATALYST CONCENTRATION =0.02170N
PERCENTAGE OF REACTION FOLLOWED = 85.31
FINAL ABSORBANCE =0.039
STANDARD ERROR OF ESTIMATE =0.01026

RUN 10 ETHYL O-METHOXYBENZOATE 55.1 DEG C.

ABSORBANCE	TIME	CALC ABSORBANCE	DIFFERENCE
0.675	420.00	0.673	0.001
0.583	840.00	0.583	-0.000
0.507	1260.00	0.506	0.000
0.446	1650.00	0.444	0.001
0.388	2040.00	0.389	-0.001
0.334	2490.00	0.335	-0.001
0.284	3000.00	0.284	-0.000
0.241	3510.00	0.240	0.000
0.208	3960.00	0.208	-0.000
0.183	4380.00	0.182	0.000
0.156	4890.00	0.156	-0.000
0.134	5400.00	0.133	0.000

LEAST SQUARES RATE CONSTANT = 0.1657E-01
CATALYST CONCENTRATION =0.02170N
PERCENTAGE OF REACTION FOLLOWED = 84.93
FINAL ABSORBANCE =0.020
STANDARD ERROR OF ESTIMATE =0.00300

RUN 11 ETHYL O-METHOXYBENZOATE 63.2 DEG C.

ABSORBANCE	TIME	CALC ABSORBANCE	DIFFERENCE
0.734	810.00	0.733	0.000
0.605	1230.00	0.601	0.003
0.541	1470.00	0.538	0.002
0.428	1950.00	0.433	-0.005
0.386	2220.00	0.385	0.000
0.346	2490.00	0.343	0.002
0.306	2760.00	0.307	-0.001
0.272	3030.00	0.275	-0.003
0.247	3300.00	0.248	-0.001
0.229	3570.00	0.224	0.004
0.196	3960.00	0.196	-0.000

LEAST SQUARES RATE CONSTANT = 0.2817E-01
CATALYST CONCENTRATION =0.01930N
PERCENTAGE OF REACTION FOLLOWED = 87.60
FINAL ABSORBANCE =0.069
STANDARD ERROR OF ESTIMATE =0.01190

RUN 12 ETHYL O-METHOXYBENZOATE 63.1 DEG C.

ABSORBANCE	TIME	CALC ABSORBANCE	DIFFERENCE
0.668	840.00	0.671	-0.003
0.500	1500.00	0.498	0.001
0.406	1980.00	0.404	0.001
0.364	2250.00	0.360	0.003
0.322	2520.00	0.323	-0.001
0.290	2790.00	0.290	-0.000
0.262	3060.00	0.261	0.000
0.236	3330.00	0.236	-0.000
0.212	3600.00	0.215	-0.003
0.191	3990.00	0.188	0.002

LEAST SQUARES RATE CONSTANT = 0.2753E-01
CATALYST CONCENTRATION =0.01930N
PERCENTAGE OF REACTION FOLLOWED = 86.94
FINAL ABSORBANCE =0.069
STANDARD ERROR OF ESTIMATE =0.01036

RUN 13 ETHYL O-METHOXYBENZOATE 64.3 DEG C.

ABSORBANCE	TIME	CALC ABSORBANCE	DIFFERENCE
0.500	480.00	0.497	0.002
0.438	690.00	0.441	-0.003
0.370	990.00	0.373	-0.003
0.333	1200.00	0.331	0.001
0.287	1470.00	0.285	0.001
0.243	1770.00	0.242	0.000
0.212	2010.00	0.213	-0.001
0.185	2310.00	0.181	0.003
0.161	2580.00	0.157	0.003
0.135	2850.00	0.137	-0.002
0.092	3630.00	0.094	-0.002
0.082	3960.00	0.080	0.001

LEAST SQUARES RATE CONSTANT = 0.2816E-01
CATALYST CONCENTRATION =0.02170N
PERCENTAGE OF REACTION FOLLOWED = 90.23
FINAL ABSORBANCE =0.020
STANDARD ERROR OF ESTIMATE =0.01508

RUN 1 ETHYL O-PHENOXYBENZOATE 27.5 DEG C.

ABSORBANCE	TIME	CALC ABSORBANCE	DIFFERENCE
0.416	1470.00	0.415	0.000
0.359	2310.00	0.358	0.000
0.325	2910.00	0.323	0.001
0.282	3750.00	0.282	-0.000
0.235	4890.00	0.236	-0.001
0.206	5790.00	0.207	-0.001
0.189	6450.00	0.189	-0.000
0.168	7350.00	0.168	-0.000
0.153	8130.00	0.153	-0.000
0.145	8640.00	0.144	0.000
0.138	9090.00	0.137	0.000

LEAST SQUARES RATE CONSTANT = 0.2848E-02
CATALYST CONCENTRATION =0.07520N
PERCENTAGE OF REACTION FOLLOWED = 85.61
FINAL ABSORBANCE =0.069
STANDARD ERROR OF ESTIMATE =0.00437

RUN 2 ETHYL O-PHENOXYBENZOATE 27.5 DEG C.

ABSORBANCE	TIME	CALC ABSORBANCE	DIFFERENCE
0.412	1500.00	0.413	-0.001
0.353	2310.00	0.356	-0.003
0.318	2940.00	0.318	-0.000
0.280	3780.00	0.275	0.004
0.228	4920.00	0.228	-0.000
0.200	5820.00	0.199	0.000
0.181	6480.00	0.181	-0.000
0.161	7380.00	0.161	-0.000
0.147	8160.00	0.146	0.000
0.138	8670.00	0.138	-0.000
0.131	9120.00	0.131	-0.000

LEAST SQUARES RATE CONSTANT = 0.3040E-02
CATALYST CONCENTRATION =0.07440N
PERCENTAGE OF REACTION FOLLOWED = 87.34
FINAL ABSORBANCE =0.069
STANDARD ERROR OF ESTIMATE =0.00877

RUN 3 ETHYL O-PHENOXYBENZOATE 34.1 DEG C.

ABSORBANCE	TIME	CALC ABSORBANCE	DIFFERENCE
0.582	330.00	0.583	-0.001
0.542	600.00	0.536	0.005
0.474	990.00	0.476	-0.002
0.426	1380.00	0.424	0.001
0.377	1800.00	0.375	0.001
0.334	2220.00	0.333	0.000
0.294	2670.00	0.295	-0.001
0.261	3120.00	0.262	-0.001
0.227	3660.00	0.228	-0.001
0.201	4200.00	0.201	-0.000
0.181	4710.00	0.179	0.001
0.162	5250.00	0.160	0.001
0.144	5820.00	0.144	-0.000

LEAST SQUARES RATE CONSTANT = 0.4713E-02
CATALYST CONCENTRATION =0.07520N
PERCENTAGE OF REACTION FOLLOWED = 87.15
FINAL ABSORBANCE =0.069
STANDARD ERROR OF ESTIMATE =0.00752

RUN 4 ETHYL O-PHENOXYBENZOATE 34.1 DEG C.

ABSORBANCE	TIME	CALC ABSORBANCE	DIFFERENCE
0.575	360.00	0.572	0.002
0.532	600.00	0.531	0.000
0.472	1020.00	0.468	0.003
0.420	1380.00	0.421	-0.001
0.372	1800.00	0.373	-0.001
0.330	2250.00	0.329	0.000
0.292	2700.00	0.291	0.000
0.258	3150.00	0.259	-0.001
0.226	3690.00	0.226	-0.000
0.199	4230.00	0.199	-0.000
0.180	4740.00	0.178	0.001
0.160	5280.00	0.160	-0.000
0.144	5850.00	0.143	0.000

LEAST SQUARES RATE CONSTANT = 0.4732E-02
CATALYST CONCENTRATION =0.07440N
PERCENTAGE OF REACTION FOLLOWED = 87.01
FINAL ABSORBANCE =0.069
STANDARD ERROR OF ESTIMATE =0.00584

RUN 5 ETHYL O-PHENOXYBENZOATE 34.0 DEG C.

ABSORBANCE	TIME	CALC ABSORBANCE	DIFFERENCE
0.545	630.00	0.544	0.000
0.484	1050.00	0.482	0.001
0.434	1410.00	0.436	-0.002
0.390	1830.00	0.389	0.000
0.347	2280.00	0.346	0.000
0.309	2730.00	0.308	0.000
0.276	3180.00	0.276	-0.000
0.244	3720.00	0.244	-0.000
0.217	4260.00	0.216	0.000
0.197	4740.00	0.196	0.000
0.177	5280.00	0.177	-0.000
0.159	5880.00	0.159	-0.000

LEAST SQUARES RATE CONSTANT = 0.4761E-02
CATALYST CONCENTRATION =0.07120N
PERCENTAGE OF REACTION FOLLOWED = 86.22
FINAL ABSORBANCE =0.079
STANDARD ERROR OF ESTIMATE =0.00347

RUN 6 ETHYL O-PHENOXYBENZOATE 44.0 DEG C.

ABSORBANCE	TIME	CALC ABSORBANCE	DIFFERENCE
0.561	1500.00	0.557	0.003
0.510	2160.00	0.511	-0.001
0.440	3360.00	0.438	0.001
0.402	4080.00	0.401	0.000
0.378	4590.00	0.377	0.000
0.344	5370.00	0.344	-0.000
0.313	6240.00	0.312	0.000
0.284	7080.00	0.286	-0.002
0.260	7980.00	0.261	-0.001
0.238	8940.00	0.239	-0.001
0.212	10380.00	0.211	0.000
0.195	11460.00	0.194	0.000
0.180	12690.00	0.179	0.000
0.163	14250.00	0.163	-0.000

LEAST SQUARES RATE CONSTANT = 0.9378E-02
CATALYST CONCENTRATION =0.01810N
PERCENTAGE OF REACTION FOLLOWED = 79.71
FINAL ABSORBANCE =0.030
STANDARD ERROR OF ESTIMATE =0.00716

RUN 7 ETHYL O-PHENOXYBENZOATE 44.0 DEG C.

ABSORBANCE	TIME	CALC ABSORBANCE	DIFFERENCE
0.597	1500.00	0.592	0.004
0.539	2190.00	0.539	-0.000
0.462	3390.00	0.461	0.000
0.423	4110.00	0.421	0.001
0.396	4620.00	0.396	-0.000
0.360	5400.00	0.361	-0.001
0.327	6270.00	0.327	-0.000
0.299	7110.00	0.298	0.000
0.270	8040.00	0.271	-0.001
0.248	8970.00	0.248	-0.000
0.219	10410.00	0.218	0.000
0.200	11490.00	0.200	-0.000
0.184	12690.00	0.184	-0.000
0.168	14280.00	0.166	0.001

LEAST SQUARES RATE CONSTANT = 0.9375E-02
CATALYST CONCENTRATION =0.01810N
PERCENTAGE OF REACTION FOLLOWED = 80.27
FINAL ABSORBANCE =0.030
STANDARD ERROR OF ESTIMATE =0.00698

RUN 8 ETHYL O-PHENOXYBENZOATE 44.1 DEG C.

ABSORBANCE	TIME	CALC ABSORBANCE	DIFFERENCE
0.446	1530.00	0.441	0.004
0.392	1920.00	0.393	-0.001
0.358	2250.00	0.357	0.000
0.328	2550.00	0.328	-0.000
0.304	2850.00	0.303	0.000
0.273	3240.00	0.273	-0.000
0.246	3630.00	0.247	-0.001
0.226	3990.00	0.227	-0.001
0.206	4410.00	0.206	-0.000
0.191	4770.00	0.190	0.000
0.177	5130.00	0.176	0.000
0.166	5490.00	0.165	0.000
0.152	5940.00	0.152	-0.000
0.144	6270.00	0.143	0.000

LEAST SQUARES RATE CONSTANT = 0.9139E-02
CATALYST CONCENTRATION =0.04060N
PERCENTAGE OF REACTION FOLLOWED = 89.87
FINAL ABSORBANCE =0.079
STANDARD ERROR OF ESTIMATE =0.00617

RUN 9 ETHYL O-PHENOXYBENZOATE 55.1 DEG C.

ABSORBANCE	TIME	CALC ABSORBANCE	DIFFERENCE
0.512	1260.00	0.514	-0.002
0.466	1650.00	0.465	0.000
0.431	1980.00	0.429	0.001
0.394	2370.00	0.392	0.001
0.362	2730.00	0.361	0.000
0.329	3150.00	0.329	-0.000
0.309	3450.00	0.309	-0.000
0.254	4500.00	0.253	0.000

LEAST SQUARES RATE CONSTANT = 0.1887E-01
CATALYST CONCENTRATION =0.01810N
PERCENTAGE OF REACTION FOLLOWED = 68.51
FINAL ABSORBANCE =0.039
STANDARD ERROR OF ESTIMATE =0.00402

RUN 10 ETHYL O-PHENOXYBENZOATE 55.1 DEG C.

ABSORBANCE	TIME	CALC ABSORBANCE	DIFFERENCE
0.334	1290.00	0.338	-0.004
0.284	1680.00	0.282	0.001
0.248	1980.00	0.249	-0.001
0.214	2400.00	0.213	0.000
0.192	2760.00	0.191	0.000
0.171	3180.00	0.171	-0.000
0.164	3480.00	0.161	0.002
0.138	4530.00	0.138	-0.000

LEAST SQUARES RATE CONSTANT = 0.1917E-01
CATALYST CONCENTRATION =0.04060N
PERCENTAGE OF REACTION FOLLOWED = 85.17
FINAL ABSORBANCE =0.039
STANDARD ERROR OF ESTIMATE =0.02737

(b) SUMMARY OF RATE CONSTANTS

Table 7

Ethyl o-Toluate

Rate Constants (measured)

Run	Temperature (°C.)	$k \times 10^3$
1	36.2	1.082
2	36.1	1.136
3	35.1	1.023
4	44.4	1.929
5	44.5	1.983
6	44.4	1.939
7	54.6	4.089
8	55.1	4.317
9	55.2	4.205
10	64.8	8.432
11	63.6	7.754
12	65.5	8.592
13	65.3	8.604

Table 8

Ethyl o-Chlorobenzoate

Rate Constants (measured)

Run	Temperature (°C.)	$k \times 10^3$
1	27.8	7.357
2	27.8	7.257
3	27.7	7.334
4	36.2	11.98
5	36.2	11.94
6	35.9	11.94
7	45.3	21.05
8	44.7	19.92
9	44.9	20.40
10	50.2	25.84
11	50.3	27.56
12	53.2	32.57

Table 9

Ethyl o-Methoxybenzoate

Rate Constants (measured)

Run	Temperature (°C.)	k x 10^3
1	36.0	3.982
2	35.8	4.069
3	35.8	4.141
4	44.6	7.753
5	44.5	7.863
6	44.3	7.677
7	52.7	13.44
8	52.8	12.86
9	55.2	16.90
10	55.1	16.57
11	63.2	28.17
12	63.1	27.53
13	64.3	28.16

Table 10

Ethyl o-Phenoxybenzoate

Rate Constants (measured)

Run	Temperature (°C.)	k x 10^3
1	27.5	2.848
2	27.5	3.040
3	34.1	4.713
4	34.1	4.732
5	34.0	4.761
6	44.0	9.378
7	44.0	9.375
8	44.1	9.139
9	55.1	18.87
10	55.1	19.17

Table 11

Ethyl o-toluate

Rate Constants by Titration Method

Run	Temperature	k x 10^4
1	25.0	3.748
2	25.0	3.664
3	35.0	9.992
4	35.0	9.866
5	45.0	18.75
6	45.0	18.97

(c) AVERAGE RATE CONSTANTS AND THERMODYNAMIC ACTIVATION PARAMETERS

Table 12

Average Rate Constants

$k \times 10^3$ ($l\ mol^{-1} sec^{-1}$)

Temperature (°C.)	25	35	45	55	65
Ethyl o-toluate		0.9880	2.100	4.268	8.324
Ethyl o-chlorobenzoate	6.100	11.33	20.28	35.05	
Ethyl o-methoxybenzoate		3.818	7.986	15.98	30.73
Ethyl o-phenoxybenzoate	2.445	5.043	9.949	18.84	

Table 13

Thermodynamic Activation Parameters

	ΔH^* (kcal/mol)	ΔS^* (cal/deg/mol)	ΔG^{*+} (kcal/mol)	r‡
Ethyl o-toluate	14.06(±0.43)	-26.70	22.56	.9994
Ethyl o-chlorobenzoate	10.71(±0.37)	-32.75	21.13	.9993
Ethyl o-methoxybenzoate	13.75(±0.59)	-25.04	21.72	.9989
Ethyl o-phenoxybenzoate	12.61(±0.36)	-28.18	21.58	.9997

+ Values of ΔG^* are calculated at 45°C.

‡ Correlation coefficients for points on the ART plots.

D I S C U S S I O N

(a) COMPARISON WITH RATES IN THE LITERATURE

Because the reactivities of ortho substituted benzoic esters are potentially complicated by steric effects, they have not received as much attention as their meta and para substituted isomers.

Literature values of rate constants (where possible at 25°C.) and Arrhenius activation parameters, measured in a variety of solvents, are listed in Table 15. For purposes of comparison, the relevant values obtained in this study, extrapolated if necessary to 25°C., are listed in Table 14.

TABLE 14

Second Order Rate Constants and Activation Parameters Measured in 60% Dioxan

	$kx10^3$(25°C)	E_a	log A
	l $mol^{-1}sec^{-1}$	kcal mol^{-1}	
Ethyl o-toluate	0.442	14.65	7.32
Ethyl o-chlorobenzoate	6.10	11.30	6.07
Ethyl o-methoxybenzoate	1.74	14.34	7.75
Ethyl o-phenoxybenzoate	2.45	13.20	7.07

TABLE 15

Rate Constants and Activation Parameters from the Literature

No.	Ortho-Substituent	Aqueous Solvent	$kx10^3$(25°C) l/mol/sec	E_a Kcal/mol	log A	Ref.
1	-H	70% dioxan	3.43	14.0	7.82	86
2	-H	56% acetone	2.89	14.56	8.18	87
3	-H	85% ethanol	0.621	17.7	-	63
4	$-CH_3$	"	0.0776	18.0	-	63
5	-Cl	"	1.39	15.7	-	63
6	-H	"	0.55	17.7	-	88
7	-H	50% ethanol	1.33	-	-	88
8	-H	40% acetone	3.80	13.75	-	66
9	-H	30% acetone	7.73	12.56	7.09	68
10	-H	40% acetone	4.63	13.13	7.30	68
11	$-CH_3$	"	0.482	13.79	6.79	68
12	-Cl	"	5.33	12.11	6.61	68
13	-H	50% acetone	3.48	13.75	7.62	68
14	$-CH_3$	"	0.357	14.46	7.16	68
15	-Cl	"	4.03	12.64	6.87	68
16	-H	60% acetone	2.88	14.50	8.09	68
17	$-CH_3$	"	0.305	14.96	7.45	68
18	-Cl	"	3.61	13.26	7.28	68
19	-H	3% ethanol	30.1	-	-	67
20	$-CH_3$	"	4.92	-	-	67
21	-Cl	"	33.5	-	-	67
22	$-OCH_3$	"	16.2	-	-	67
23	$-NO_2$	"	33.4	-	-	67
24	-H	65% DMSO	34.5	-	-	89
25	$-CH_3$	"	5.79	-	-	89
26	-Cl	"	67.0	-	-	89

No.	Ortho-Substituent	Aqueous Solvent	$kx10^3$(25°C) l/mol/sec	E_a kcal/mol	log A	Ref.
27	$-OCH_3$	65% DMSO	10.7	-	-	89
28	$-NO_2$	"	295	-	-	89
29	-H	85% DMSO	166	-	-	89
30	$-CH_3$	"	28.9	-	-	89
31	-Cl	"	358	-	-	89
32	$-OCH_3$	"	27.8	-	-	89
33	$-NO_2$	"	2390	-	-	89
34	-H	95% DMSO	1150	-	-	89
35	$-CH_3$	"	358	-	-	89
36	-Cl	"	3810	-	-	89
37	$-OCH_3$	"	199	-	-	89
38	-H	20% dioxan	5.9 (20°C)	-	-	71
39	$-OCH_3$	"	1.9 (20°C)	-	-	71
40	$-CH_3$	60% dioxan	0.880 (35°C)	13.98	6.8	70
41	$-CO-C_6H_5$	"	35.0	9.32	5.4	70
42	$-C_6H_5$	"	0.197 (45°C)	16.43	7.6	70
43	-H	85% ethanol	1.39 (35°C)	18.4	10.2	62
44	$-CH_3$	"	0.203 (35°C)	19.5	10.1	62
45	-Cl	"	2.81 (35°C)	16.6	9.2	62
46	$-CH_3$	60% dioxan	1.46	14.3	7.7	62
47	-H	"	11.8	13.6	8.0	62

(methyl esters)

The only compound in Table 15 which is directly comparable with the results obtained in this project is ethyl o-toluate (No. 40), whose rate was studied in 60% dioxan by B.C. Chauncy [70] using a resistance technique. His value of 0.880×10^{-3} l $mol^{-1}sec^{-1}$ at 35°C. is somewhat lower than the value 0.998×10^{-3} l $mol^{-1}sec^{-1}$ obtained here using the spectrophotometric technique. The average value obtained in this project by the titration technique is 0.989 l $mol^{-1}sec^{-1}$, which is in good agreement with the spectrophotometric result.

Some comparison of the rates obtained in this project with the rates obtained by previous workers can be made by considering relative rates in different solvents. Table 16 lists the relative rates obtained in this project at 25°C., and relative rates that have been reported in the solvents indicated.

TABLE 16

Relative Rates in Various Aqueous Solvents (25°C.)

Ortho-Substituent	60% Dioxan+	85% Ethanol[63]	3% Ethanol[67]	40% Acetone[68]	65% DMSO[89]
$-CH_3$	1.00	1.00	1.00	1.00	1.00
-Cl	14.4	17.9	6.81	11.1	12.7
$-OCH_3$	4.11	-	3.29	-	1.85

+ Results obtained in this project.

It can be seen that the relative rates obtained in this project are reasonably well supported by the relative rates obtained in other solvents. As pointed out by Kondo et. al. [90], substituent effects in one solvent are not directly comparable with substituent effects in another solvent, since they are also affected by the interaction between individual substituents and solvents.

The relative rate of the ortho-chloro substituted compound is low in 3% ethanol, and this could be caused by strong solvation of the electronegative chlorine atom by the highly polar aqueous solvent, producing a secondary steric effect. This will be discussed later.

(b) ASSESSMENT OF SUBSTITUENT EFFECTS ON THE RATE CONSTANTS (FREE ENERGIES)

Newman and Leegwater [28] have presented evidence that certain ortho-substituted esters undergo alkaline hydrolysis via an intramolecular (neighbouring group assistance) mechanism. The substituents studied in the present work, however, would all be expected to hydrolyse via the normal $B_{AC}2$ mechanism (see page 11). In this mechanism substituent effects are quite unambiguous: electron-attracting substituents would be expected to accelerate the reaction by making the carbonyl carbon of the ester more prone to attack by the OH^- reagent, while increasing steric bulk of substituents would

decrease the rate of reaction by increasing the crowding in the SP^3 transition state relative to the original ester.

The relative rates at 45°C. of the four compounds studied are listed in Table 17.

TABLE 17

Relative Rates at 45°C.

Compound	Relative Rate
Ethyl o-toluate	1.00
Ethyl o-chlorobenzoate	9.66
Ethyl o-methoxybenzoate	3.80
Ethyl o-phenoxybenzoate	4.73

The high reaction velocity of the chloro substituted compound is predictable in view of the fact that it is more strongly electron withdrawing than the methyl group.

The ortho-methoxy group does not attract electrons as strongly as the ortho-methyl group, which should cause it to react more slowly, but its steric effect is also much less than that of the methyl group, and this tends to oppose the polar effect. Taft (Table 1, page 17) lists

$\sigma^*_{(methyl)} = 0.00$ $\quad E_{s(methyl)} = 0.00$

$\sigma^*_{(methoxy)} = -0.22$ $\quad E_{s(methoxy)} = +0.99$

and substitution of these figures in the Taft equation indicates

that the methoxy compound would be expected to hydrolyse approximately six times as fast as ethyl o-toluate at 25°C.

The rate of hydrolysis of ethyl o-phenoxybenzoate is marginally greater than that of ethyl o-methoxybenzoate. Other rate constants for this compound are not available in the literature. Jaffe [40] lists the para-substituent constants as σ_p (methoxy) = -0.27, σ_p (phenoxy) = -0.003, which indicates that, from polar considerations alone, the phenoxy compound should react faster than the methoxy compound. However, the phenoxy compound could be expected to exert a considerable steric effect relative to the methoxy group, which it apparently does not do. The steric effect of the phenyl group is known to be large [70], but the above results would indicate that the bulk of the substituent benzene ring does not hinder the reaction centre when it is once removed by an oxygen bridge from the substrate benzene ring. This conclusion is reinforced by the relative steric factors of the methyl and methoxy groups.

The E_s value listed above (+0.99) for the methoxy group relative to the methyl group, and the apparent lack of steric hindrance observed for the phenoxy group, require some consideration in terms of the Taft treatment of ortho substituent effects. It does not seem reasonable that the steric effect of the methoxy group should be so vastly different to that of the methyl group. This difference cannot

be explained in terms of possible conjugation of the methoxy group, which would tend to increase the energy of activation required to form the unconjugated transition state. In support of this, the ultra-violet spectra of the methoxy and phenoxy compounds do not exhibit any evidence of substituent conjugation i.e. they do exhibit $0 \rightarrow 0$ transitions.

It is possible that what is being observed here is the result of hyperconjugation of the methyl group with the benzene ring in ethyl o-toluate. Such hyperconjugation would decrease the rate of hydrolysis of ethyl o-toluate (the reference compound) compared to the unconjugated o-methoxy compound, which is the effect observed in this instance.

(c) ASSESSMENT OF SUBSTITUENT EFFECTS ON THE ENTHALPIES OF ACTIVATION

The enthalpy of activation in an alkaline ester hydrolysis proceeding via a $B_{AC}2$ mechanism is probably largely a function of the attraction between the hydroxyl ion and the carbonyl carbon atom [91], and factors which facilitate the formation of the transition state by decreasing its potential energy tend to lower ΔH^*.

For unsubstituted benzoic esters, the major factor producing variation in ΔH^* is the nature of the solvent. A solvent which is capable of solvating the reaction site

stabilises the transition complex and lowers enthalpy of activation. Since

$$\Delta G^* = \Delta H^* - T\Delta S^* ,$$

this effect tends to be compensated by the decrease of ΔS^* resulting from increased solvation, and the overall effect on ΔG^* is not as great [92].

When a substituent is introduced into the ortho position, a number of factors have to be considered.

The inductive effect exerted by the substituent alters the partial charge on the carbonyl carbon atom. An electron withdrawing substituent causes a decrease in ΔH^*, and this is somewhat compensated by polar facilitation of solvation, which decreases ΔS^*. A substituent which is more electron repelling than a hydrogen atom increases ΔH^*.

If resonance interaction [93] exists between the substituent, the benzene ring, and the functional carbonyl group, then extra energy is required to form the tetrahedral transition complex, which does not conjugate as strongly as the substrate, and ΔH^* is increased.

A bulky ortho-substituent may sterically hinder conjugation between the benzene ring and the carbonyl group in the reactant molecule [62], so that less energy is required to form the transition complex, and ΔH^* is lowered.

The major steric effect of a bulky substituent [93] is to increase the bond strain in the transition state due to repulsion between the substituent, the reaction centre and the hydroxyl ion. This increases the enthalpy of activation.

A bulky substituent may also inhibit solvation of the transition complex. Steric inhibition of solvation serves to increase ΔH^*, although the effect of this increase on reaction rate is compensated by the consequent increase of ΔS^*.

Values of ΔH^* obtained for the compounds studied were (in kcal mol^{-1}) (1) ethyl o-toluate (14.06), (2) ethyl o-chlorobenzoate (10.71), (3) ethyl o-methoxybenzoate (13.75) and (4) ethyl o-phenoxybenzoate (12.61). For purposes of comparison, an acceptable value of ΔH^* for ethyl benzoate is 13.4 kcal mol^{-1} [86].

In considering substituent effects on ΔH^*, the changes in ΔH^* produced by the substituents relative to ethyl benzoate are listed in Table 18.

TABLE 18

Substituent Effects on ΔH^*

Substituent	$\delta\Delta H^*$ (kcal mol^{-1})
$-CH_3$	+0.6
-Cl	-2.7
$-OCH_3$	+0.4
$-OC_6H_5$	-0.8

These results are consistent with what would be predicted in terms of the polar nature of substituents. ΔH^* has been increased slightly by the methyl and methoxy groups, and has been decreased by the chloro and phenoxy substituents.

The decrease of 2.7 kcal mol^{-1} recorded for the chloro substituent is somewhat larger than would have been expected from comparison with values obtained in other solvents, and will be discussed further in section (f).

It may also be noted that the greater electron attracting power of the phenyl group in comparison with the methyl group causes ΔH^* for the phenoxy substituent to be significantly lower than for the methoxy substituent.

(d) ASSESSMENT OF SUBSTITUENT EFFECTS ON THE ENTROPIES OF ACTIVATION

Entropies of activation for the saponification of ethyl benzoates range from -15 to -35 cal K^{-1} mol^{-1} [94,95], depending on the nature of the solvent and substituents.

Entropy variations can be classified into those which are common to ester saponification reactions, and those which are produced by a substituent.

The major contribution to ΔS^* is that due to solvation of the transition state. The "freezing out" of solvent molecules lowers the entropy of the solvent system.

The degree of solvation of the reaction site can be affected by substituents on the benzene ring. An electron withdrawing substituent in the ortho or para positions increases the field at the reaction centre, and causes ΔS^* to be more negative through increased solvation.

Entropy of activation is also dependent on the polar nature of the solvent, and this aspect will be discussed in section (g).

The effects of ortho substituents on entropy of activation can be divided into two main areas. The first involves the steric effect of the substituent on the vibrational motions of the transition complex. A bulky substituent hinders the vibrational modes available to the transition state relative to an umsubstituted transition state, decreasing entropy of activation. If the nature of the substituent is such that steric strain hinders vibrations of the substituent itself, a decrease in ΔS^* is produced also [97].

The second substituent effect is steric inhibition of solvation. If the bulk of the substituent group inhibits solvation of the reaction site, entropy of activation is increased. Steric inhibition of solvation opposes the increased solvation produced by an electron withdrawing substituent in the ortho position, and it also opposes the substituent bulk effect on entropy of activation.

The values of ΔS^* (in cal K^{-1} mol^{-1}) obtained in this project were (1) ethyl o-toluate (-26.7),

(2) ethyl o-chlorobenzoate (-32.7), (3) ethyl o-methoxybenzoate (-25.0), and (4) ethyl o-phenoxybenzoate (-28.2).

Price [86] found ΔS^* for ethyl benzoate to be -24.6 cal K^{-1} mol^{-1} in 70% dioxan, and in 60% dioxan it would be expected to be slightly more positive than this.

The substituent entropy effects $\delta\Delta S^*$ relative to the value given by Price are listed in Table 19.

TABLE 19

Substituent Effects on ΔS^*

Substituent	$\delta\Delta S^*$ (cal K^{-1} mol^{-1})
$-CH_3$	-2.1
$-Cl$	-8.1
$-OCH_3$	-0.4
$-OC_6H_5$	-3.6

The decrease in ΔS^* caused by the methyl group would not be expected from polar considerations, and could be attributed to the steric bulk effect of the methyl group causing hindered vibration in the transition state relative to the unsubstituted transition state. This suggestion is reinforced by the significantly smaller effect produced by the methoxy group, whose steric effect has been noted previously to be less than that of the methyl group.

The large decreases in ΔS^* encountered in the

chloro and phenoxy substituted compounds can be attributed to polar facilitation of solvation of the transition complex, since both of these substituents are electron attracting.

(e) SOLVENT EFFECTS ON THE RATE CONSTANTS

The rate of saponification of an ester by the $B_{AC}2$ mechanism can be expected to increase with the polarity of the solvent, since solvation of the ionic transition state by the solvent molecules tends to decrease enthalpy of activation.

From empirical considerations [96]

$$\log k \propto \frac{1}{\varepsilon} ,$$

where k is the second order rate constant for the reaction and ε is the dielectric constant of the solvent.

Table 20 lists second order rate constants at 25°C. for the compounds indicated in various aqueous solvents whose dielectric constants are also listed.

SOLVENT VARIATION OF RATE CONSTANTS

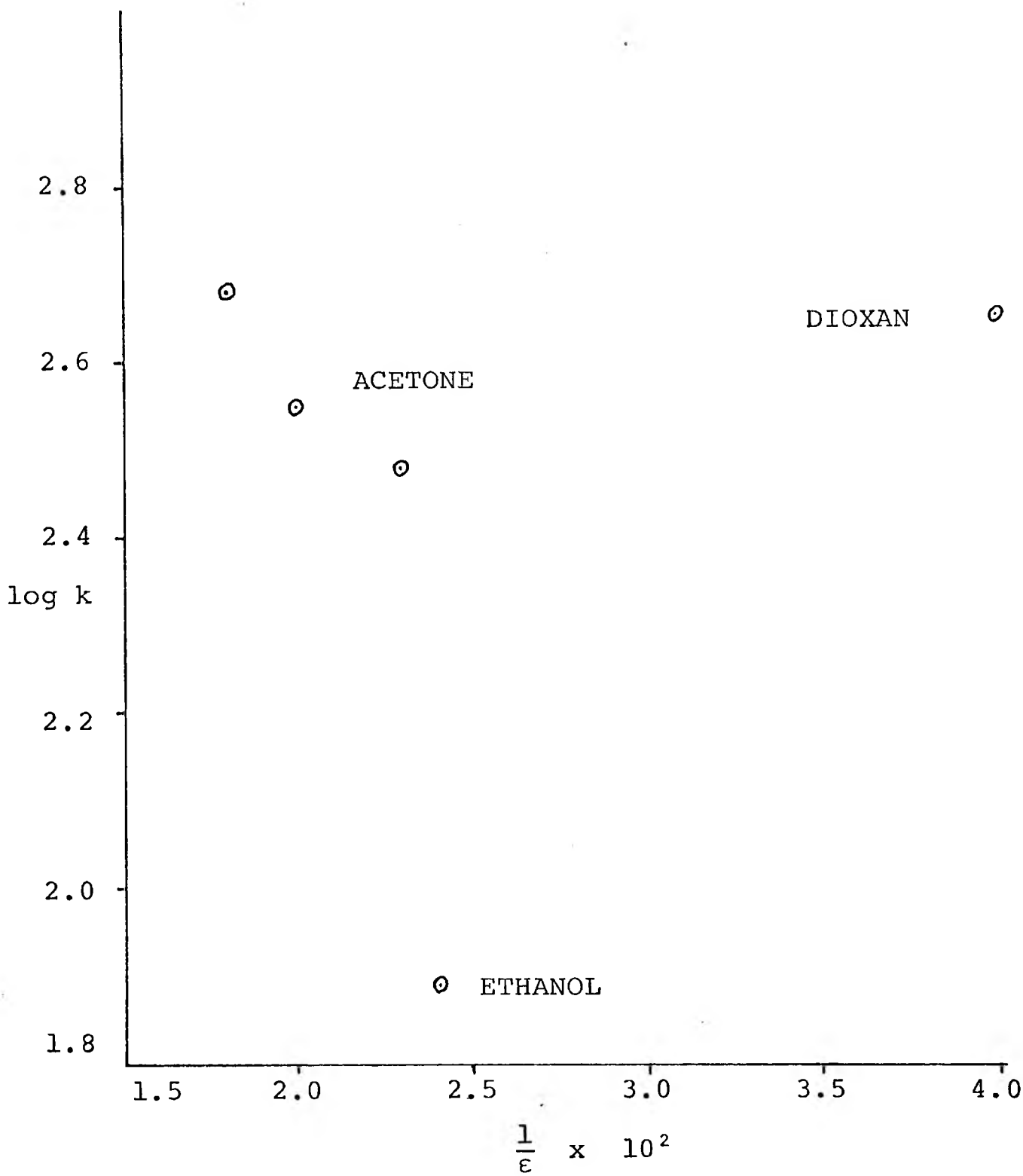


FIGURE 18

TABLE 20

Variation of Rate Constant with Solvent

(Substituted ethyl benzoates)

Ortho substituent	ε	$k \times 10^3$ (25°C.) ($l\ mol^{-1}\ sec^{-1}$) -H	-CH_3	-Cl	Ref.
70% dioxan	18	3.43	-	-	86
60% dioxan	25	-	0.442	6.10	This project
85% ethanol	41	0.621	0.0776	1.39	63
60% acetone	44	2.88	0.305	3.61	68
50% "	49	3.48	0.357	4.03	68
40% "	55	4.63	0.482	5.33	86
30% "	61	7.73	-	-	68

From the values listed in Table 20 it can be seen that while variations within a solvent (acetone) are in good agreement with theoretical predictions, comparisons with other solvents do not appear to be valid. This same situation has been noted for other reactions [96]. Reaction rates in aqueous dioxan are high in comparison with acetone, and rates in aqueous ethanol are low.

The values of log k are plotted against $\frac{1}{\varepsilon}$ for ethyl o-toluate in Figure 18. The distribution of points in this scattergram is similar to that obtained for the other two substituents.

These results are probably an indication of the degree to which the polar component of an aqueous mixture may be separated from the non-polar component in solvating the transition state. It is probable that the polar ethanol and acetone molecules are themselves hydrated by water molecules, whereas the non-polar dioxan molecules are not, so that the effective concentration of free water molecules in aqueous dioxan mixtures is relatively greater than expected. "Solvent sorting" will be discussed further in section (g).

(f) SOLVENT EFFECTS ON THE ENTHALPIES OF ACTIVATION

For reasons discussed in section (e), values of ΔH^* for a given compound can be expected to decrease as the solvent becomes more polar. Table 21 lists ΔH^* values relative to ethyl benzoate produced by the methyl and chloro substituents in various solvents whose dielectric constants are indicated.

TABLE 21

Solvent Variations of ΔH^*

Solvent	ε	$\Delta H^*_{CH_3}$	ΔH^*_{Cl}	Ref.
		(k cal mol^{-1})		
60% dioxan	25	+0.6	-2.7	This project
85% ethanol	41	+4.0	-2.0	63
60% acetone	44	+1.0	-1.2	68
50% acetone	49	+0.5	-1.1	68
40% acetone	55	-0.2	-1.0	68

From Table 21 it may be seen that for ethyl o-toluate the solvent effects are in accord with predictions except for the anomalous position of the dioxan solvent which has been noted in section (e). However, the ortho-chlorobenzoate exhibits higher values of ΔH^* in more polar solvents, completely reversing the predicted trend.

A possible explanation of this could be developed from a suggestion by Chapman [62] that strong solvation of the electronegative chlorine atom may produce a secondary steric effect at the reaction site. Such solvation would cause ΔH^* to be relatively increased, and the effect would be more marked in polar solvents.

(g) SOLVENT EFFECTS ON THE ENTROPIES OF ACTIVATION

Entropy of activation is also dependent on the polar nature of a solvent, since a more polar solvent will more efficiently solvate the reaction site in the transition complex, causing ΔS^* to be decreased.

Table 22 lists entropies of activation in different aqueous solvents for the saponification of ethyl benzoate. The values of ΔS^* were calculated from the published data.

TABLE 22

Solvent Variation of ΔS^* for Ethyl Benzoate

Aqueous Solvent	ε	ΔS^* (cal k^{-1} mol^{-1})	Ref.
70% dioxan	18	-24.6	86
85% ethanol	41	-15.6	63
56% acetone	46	-21.0	87
40% acetone	55	-25.3	86
30% acetone	61	-27.8	68

In the mixed aqueous solvents in Table 22, the values of ΔS^* show a decreasing trend in solvents with a larger dielectric constant (i.e. more polar solvents), the only exception again being the value for aqueous dioxan.

A second solvent contribution to entropy of activation is the effect of "solvent sorting" [98]. If the more polar, e.g. water, molecules of a binary solvent system are attracted to reaction sites, the solvent becomes partially ordered, and contributes a negative effect to ΔS^*. The low value noted for ΔS^* in aqueous dioxan in Table 22 can be attributed to solvent sorting. The dioxan molecule has a zero dipole moment, and its solution in water would be more prone to the separation of the polar water molecules than would solutions of the more polar ethanol and acetone molecules.

(h) THE ISOKINETIC RELATIONSHIP

Exner [45] has shown from statistical considerations that when the activation parameters are calculated from rate data, the error contours of the rate data are multiplied by a factor which is practically constant over a small temperature range. This effect can produce linearity in a set of random results, or can make a set of linear points appear to be randomly distributed in a plot of ΔH^* against ΔS^*. He advocates that the isokinetic plot should be preceded by a log plot of rate data at two different temperatures, i.e., log k_1 against log k_2, which if linear implies a true isokinetic relationship for the series of compounds.

The rate constants obtained for the compounds studied in this project have been plotted according to Exner's technique by plotting log k_{55}° against log k_{25}° for each compound. These are represented by points 1-4 in Figure 19.

For purposes of comparison, results obtained by Chauncy [70] for three compounds he studied in 60% dioxan are represented by points 5-7.

The linear nature of the graph in Figure 19 indicates that an isokinetic relationship does exist for the reaction series under consideration, and a plot of ΔH^* against ΔS^* gives a line of best fit whose slope $\beta = 530^{\circ}K$.

ISOKINETIC PLOT

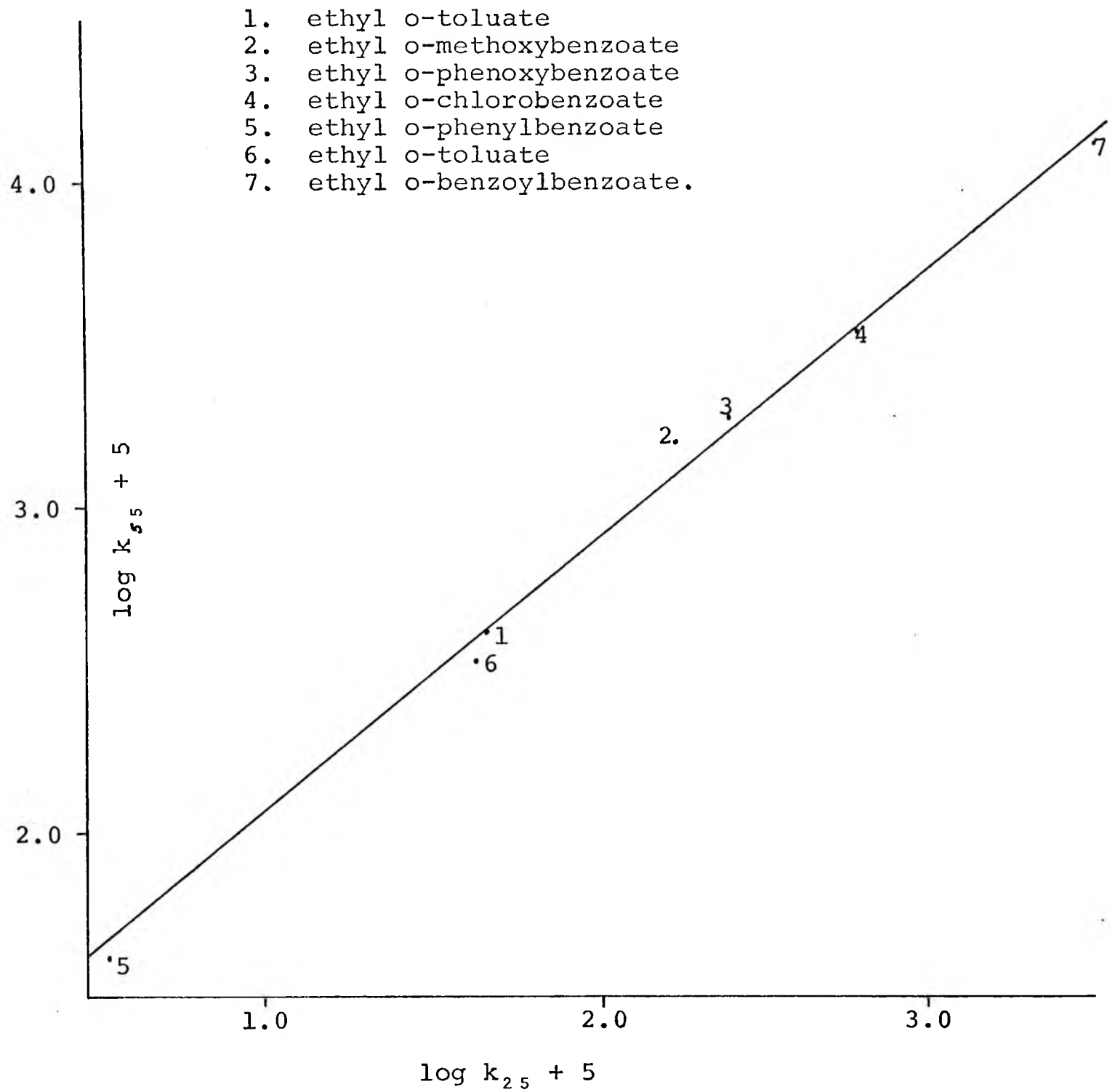


FIGURE 19

This isokinetic temperature lies well outside the range of experimental temperatures and it can be concluded that the relative rates of the reactions studied were in the region of control of ΔH^*.

This can also be taken as evidence that these compounds all react by the same mechanism.

(i) THE SPECTROPHOTOMETRIC TECHNIQUE

One of the aims of this project was to examine the usefulness of the spectrophotometric technique in studying the kinetics of hydrolysis of ortho-substituted esters. The intensity of the ultraviolet absorption peaks of these compounds is such that the ester has to be used in a low concentration, and the necessity of having a reaction 75% complete in a few hours requires that the (OH^-) concentration be relatively large, so that it is not possible to avoid the use of a pseudo first order kinetic method. This has both advantages and disadvantages.

(i) Advantages

Advantages of the technique are that concentration may be measured accurately and quickly, with a minimum of physical disturbance to the system being studied. It may be noted that care should be taken that a reaction cell is not kept in the ultraviolet beam for longer than necessary, as the radiation itself may be able to exert a

catalytic effect on the reaction.

Another advantage is that this technique allows the use of small reaction samples, with economy of reactants and solvents.

With the use of first order kinetics it is not necessary to be able to relate absorbance to concentration of reactant, since it is not necessary to know initial absorbance to calculate the rate constant.

(ii) Disadvantages

One disadvantage of this technique is that it is not suitable for use on some compounds. This will be discussed in section (iv).

Because the products of the reactions (in this case the anions) are also absorbing species, it is not possible to obtain a true infinity absorbance reading, and error caused by residual anion absorbance has to be allowed for.

Any technique which employs very low reactant concentrations, as this does, is susceptible to errors produced by the presence of impurities in the reactants or solvent, and care must be taken to eliminate these impurities. As described previously, problems were experienced in this project due to the presence of the impurity 2-methyl-1, 3-dioxolane in the solvent, which produced an absorbing species by reacting with the sodium hydroxide solution during the reaction, and a

different method of dioxan purification had to be employed to eliminate this impurity.

Because of the low reactant concentrations employed it was impossible to isolate and identify the products of the reactions studied, a step which is considered desirable in a kinetic investigation.

Finally, care must be taken that the catalyst solution is accurately standardised, as an error in the catalyst concentration is transferred reciprocally to the second order rate constant.

(iii) Effect of Ionic Medium

A factor which is not readily allowed for in kinetic studies is the variation of the ionic medium during the course of the reaction.

Changes in the ionic medium of the reaction can affect reaction rate, but these changes are minimised in this reaction because only a small fraction of the hydroxyl ion present is used during the course of a reaction.

Related to this is the fact that from considerations of kinetic theory it would be more accurate to assess effective catalyst concentration, which is the activity of the hydroxyl ion present, rather than hydroxyl ion concentration, but the problems involved in measuring the hydroxyl ion activity coefficients in solutions of varying concentrations

are such that the total hydroxyl ion concentration is used in calculating rate constants.

(iv) Compounds Not Suited to This Technique

Five of the compounds investigated in this project were found to be unsuitable for study by the spectrophotometric technique. The reason for their unsuitability is that their spectra (pages 48-52) do not contain absorption peaks suitable for measuring concentration change.

Apart from ethyl benzoate, whose peak does not shift sufficiently in the transition from ester to anion, all the compounds involved have ortho-substituents which resonate with the benzene ring. The peaks due to their $0 \rightarrow 0$ transitions are apparently subjected to a hypsochromic shift, and are masked by the more intense absorption of the benzene ring.

In this context it is somewhat surprising that Newman and Leegwater [28] have reported the results of a study of the saponification of ethyl o-acetylbenzoate and ethyl o-benzoylbenzoate by the use of a spectrophotometric technique.

They state that they followed the reactions by measuring the increase in anion absorbance at a wavelength of 310 mμ, in 30% dioxan-water solvent. The spectra of these two compounds on pages 49 and 51 have been carefully obtained, and it is hard to see how this technique could be useful on

these compounds unless an appreciable red shift is caused by the change in dioxan concentration from 60% to 30%.

(v) Comments on Results Obtained

It is felt that the kinetic results obtained by use of this technique are quite well-founded. Figure 13 on page 69 illustrates the linearity of the first order plot obtained for a typical run. The correlation coefficients obtained for the ART plots (page 119) were 0.9994, 0.9993, 0.9989, and 0.9997. The worst of these plots is illustrated in Figure 17 on page 87. Considering that the correlations above are based on only 10 to 13 points per correlation, the results obtained appear to be quite reliable.

(j) SUMMARY OF RESULTS

It is considered that good kinetic results can be obtained using aqueous dioxan as a solvent. For the study of alkaline hydrolysis reactions the method of purification of dioxan used by Kraus and Vingee and other workers is not recommended.

The anomalous rate constants and thermodynamic parameters obtained with dioxan in comparison with solvents of other polarities indicate that for application of results to the Taft treatment of ortho substituent effects, both acid and alkaline catalysed rates should be measured in

aqueous dioxan.

There appears to be some cause to doubt Taft's assumption that polar and steric substituent effects are independent of each other for ortho substituents, and this can only be resolved by calculating Taft parameters from ester hydrolysis data in a common solvent.

The spectrophotometric technique is an experimentally useful technique, but does not appear to be suitable for use with substituents that conjugate with the benzene ring.

(k) SUGGESTIONS FOR FURTHER RESEARCH

Other compounds that could be studied by this technique include compounds whose ortho-substituents are alkyl, hydroxy, alkoxy and halogen groups.

It would also be possible to study the kinetics of the acid catalysed hydrolysis of these compounds, with a view to calculating Taft parameters for their polar and steric effects.

This technique is not suitable for the study of conjugated ortho-substituted compounds in 60% dioxane. However, it could be worthwhile to examine the spectra of these compounds in a more polar solvent, which may shift a hidden peak towards the red end of the spectrum. This

suggestion, however, is not put forward with much optimism.

A P P E N D I X

Computer Programs

```
C  C
C       FIRST DATA CARD CONTAINS IDENTIFICATION
C       SECOND DATA CARD CONTAINS CALK VFAC ACELL AFIN
C       THIRD DATA CARD BEGINS TIME ABN PAIRS
C       A NEGATIVE TIME IS REQUIRED ON THE LAST DATA CARD
        DIMENSION ABN(40),TIME(40),X(40),Y(40),CALAB(40),DIF(40)
        DIMENSION F(43),BA(40),BB(40),BC(40),BD(40)
        WRITE(3,1)
 1      FORMAT(1H1)
   81   FORMAT(////)
  333   READ(2,200)
        WRITE(3,200)
  200   FORMAT(12X,50H
        WRITE(3,41)
   41   FORMAT(/)
        READ(2,201)CALK,VFAC,ACELL,AFIN
  201   FORMAT(4F10.3)
        DO77J=1,40
        READ(2,20) TIME(J),ABN(J)
   20   FORMAT(2F10.3)
        IF(TIME(J))70,7,7
    7   TIME(J)=TIME(J)*60.
        X(J)=TIME(J)
   77   Y(J)=ALOG(ABS(ABN(J)-ACELL-AFIN))
   70   N=J-1
        IF(ABN(1)-AFIN)8,9,9
    8   CONST=-1.
        GOTO10
    9   CONST=1.
   10   SUMX=0.
        SUMY=0.
        SUMXY=0.
        SUMXX=0.
        DO12J=1,N
        SUMX=SUMX+X(J)
        SUMY=SUMY+Y(J)
        SUMXX=SUMXX+X(J)**2
   12   SUMXY=SUMXY+X(J)*Y(J)
        G=N
        DENOM=SUMX**2-G*SUMXX
        SLOPE=(SUMX*SUMY-G*SUMXY)/DENOM
        B=(SUMX*SUMXY-SUMY*SUMXX)/DENOM
        FSUM=0.
        DO21J=1,N
        F(J)=Y(J)-SLOPE*TIME(J)-B
   21   FSUM=FSUM+F(J)*F(J)
        DEV=SQRT (FSUM/G)
C       START VARIATION IN AFIN
        AINC=.01
        LA=0
        VMOD=AFIN
```

```
      TEST=DEV
      VMOD=VMOD+AINC
      SUMX=0.
      SUMY=0.
      SUMXY=0.
      SUMXX=0.
      DO22J=1,N
      Y(J)=ALOG(ABS(ABN(J)-VMOD-ACELL))
      SUMX=SUMX+X(J)
      SUMY=SUMY+Y(J)
      SUMXX=SUMXX+X(J)*X(J)
   22 SUMXY=SUMXY+X(J)*Y(J)
      DENOM=SUMX*SUMX-G*SUMXX
      SMOD=(SUMX*SUMY-G*SUMXY)/DENOM
      BMOD=(SUMX*SUMXY-SUMY*SUMXX)/DENOM
      FSUM=0.
      DO23J=1,N
      F(J)=Y(J)-SMOD*X(J)-BMOD
   23 FSUM=FSUM+F(J)*F(J)
      DEV=SQRT(FSUM/G)
      LA=LA+1
      BA(LA)=SMOD
      BB(LA)=BMOD
      BC(LA)=VMOD
      BD(LA)=DEV
      IF(TEST-DEV)34,34,25
   25 TEST=DEV
      DO26L=1,10
      VMOD=VMOD+AINC
      SUMY=0.
      SUMX=0.
      SUMXX=0.
      SUMXY=0.
      DO29J=1,N
      Y(J)=ALOG(ABS(ABN(J)-VMOD-ACELL))
      SUMY=SUMY+Y(J)
      SUMX=SUMX+X(J)
      SUMXX=SUMXX+X(J)*X(J)
   29 SUMXY=SUMXY+X(J)*Y(J)
      DENOM=SUMX*SUMX-G*SUMXX
      SMOD=(SUMX*SUMY-G*SUMXY)/DENOM
      BMOD=(SUMX*SUMXY-SUMY*SUMXX)/DENOM
      FSUM=0.
      DO30J=1,N
      F(J)=Y(J)-SMOD*X(J)-BMOD
   30 FSUM=FSUM+F(J)*F(J)
      DEV=SQRT(FSUM/G)
      LA=LA+1
      BA(LA)=SMOD
      BB(LA)=BMOD
      BC(LA)=VMOD
```

```
      BD(LA)=DEV
      IF(TEST-DEV)345,345,26
   26 TEST=DEV
      GOTO31
   31 WRITE(3,32)
   32 FORMAT(2X,'THE CURVATURE STILL REMAINS')
      GOTO333
  345 LA=LA-1
      SLOPE=BA(LA)
      B=BB(LA)
      VMOD=BC(LA)
      TEST=BD(LA)
      AFIN=VMOD
      GOTO34
   34 RATE=ABS (SLOPE)
      SECK=RATE/CALK
      SECK=SECK*VFAC
      ABIN=AFIN+ACELL+EXP (B)*CONST
      PCENT=(ABIN-ABN(N))/(ABIN-AFIN)*100.
      WRITE(3,27)
   27 FORMAT(7X,'ABSORBANCE      TIME      CALC ABSORBANCE      DIF
     1CE')
      DO13J=1,N
      CALAB(J)=AFIN+ACELL+EXP (SLOPE*TIME(J)+B)*CONST
      DIF(J)=ABN(J)-CALAB(J)
   13 WRITE(3,14)ABN(J),TIME(J),CALAB(J),DIF(J)
   14 FORMAT(7X,F7.3,6X,F8.2,7X,F7.3,11X,F7.3)
      WRITE(3,41)
      WRITE(3,15)SECK
   15 FORMAT(12X,'LEAST SQUARES RATE CONSTANT       ='E11.4)
      WRITE(3,18)CALK
   18 FORMAT(12X,'CATALYST CONCENTRATION            ='F7.5,'N')
      WRITE(3,19)PCENT
   19 FORMAT(12X,'PERCENTAGE OF REACTION FOLLOWED   ='F6.2)
      WRITE(3,35)AFIN
   35 FORMAT(12X,'FINAL ABSORBANCE                  ='F5.3)
      WRITE(3,36)TEST
   36 FORMAT(12X,'STANDARD ERROR OF ESTIMATE        ='F7.5)
      WRITE(3,81)
      PAUSE
      GOTO333
      END
```

PAGE 2

```
C  C  KJ MCCARTHY
C     FIRST DATA CARD CONTAINS IDENTIFICATION
C     SECOND DATA CARD CONTAINS AO BO TNORM
C     THIRD DATA CARD CONTAINS ALIQUOT EACID
C     FOURTH DATA CARD CONTAINS VOLUME CORRECTION FACTOR IORD
C      FIFTH DATA CARD BEGINS TIME-TITRATION PAIRS
C     A NEGATIVE TIME IS REQUIRED ON THE LAST DATA CARD
C     IF AO=0  CONCENTRATIONS OF REACTANTS ARE EQUAL
      PRINT 81
   81 FORMAT(////)
       DIMENSION TIME(40),CONC(40),RK(40),CRK(40),X(40),Y(40)
  333 READ 200
      PRINT 200
  200 FORMAT(40H                                        )
      PRINT 41
   41 FORMAT(/)
      C=0.
      SD=0.
      SUM=0.
       S=0.
       CORR=0.
       READ 11,AO,BO,TNORM
      READ 11,ALIQ,EACID
   11 FORMAT(4F10.3)
      READ 177,VFAC,IORD
  177 FORMAT(F10.3,I1 )
      DO25 I=1,40
      READ 20 ,TIME(I),TITN
   20 FORMAT(6F10.3)
      IF(TIME(I))70,28,28
   28 GO TO (24,25,24),IORD
   24 CONC(I)=TITN*TNORM/ALIQ
      GO TO 7
   25 CONC(I)=BO+(TITN*TNORM)/ALIQ-EACID/ALIQ
    7 CONTINUE
   70 N=I-1
      AN=N
      SRSQ=0.
      IF(AO)201,201,113
  113 GO TO (777,777,778),IORD
  777 DO 13 I=1,N
      Y(I)=1./(AO-BO)*LOGF((BO*(AO-CONC(I)))/(AO*(BO-CONC(I))))
      RK(I)=Y(I)/TIME(I)
      RK(I)=RK(I)*VFAC
      SRSQ=SRSQ+RK(I)**2
      X(I)=TIME(I)
   13 SUM=SUM+RK(I)
      GO TO 171
  201 DO 21 I=1,N
       Y(I)=CONC(I)/(BO*(BO-CONC(I)))
      RK(I)=Y(I)/TIME(I)
```

```
      RK(I)=RK(I)*VFAC
      SRSQ=SRSQ+RK(I)**2
      X(I)=TIME(I)
   21 SUM=SUM+RK(I)
      GO TO 171
  778 DEL=ABSF(BO-AO)
      F=1.-DEL*DEL/((2.*AO+DEL)*(2.*(AO-CONC(N))+DEL))
      DO 15 I=1,N
      Z=1./((AO+DEL/2.)-CONC(I)) -1./(AO +DEL/2.)
      RK(I)=Z/(F*TIME(I))
      RK(I)=RK(I)*VFAC
      SRSQ=SRSQ+RK(I)**2
      Y(I)=1./(AO+DEL/2.-CONC(I))
      X(I)=TIME(I)
   15 SUM=SUM+RK(I)
  171 AVE=SUM/AN
       PN=N
       SX=0.
       SY=0.
       SXSQ=0.
       SXY=0.
       SYSQ=0.
  917   DO 199 I=1,N
       SX=SX+X(I)
       SY=SY+Y(I)
       SYSQ=SYSQ+Y(I)*Y(I)
       SXY=SXY+X(I)*Y(I)
  199  SXSQ=SXSQ+X(I)*X(I)
       PA=SXSQ-(SX*SX)/PN
       QA=SYSQ-(SY*SY)/PN
       BA=SXY-(SX*SY)/PN
       S=BA/PA
       CORR=SQRTF((BA*BA)/(PA*QA))
   22 SD=SQRTF((SRSQ/PN)-(AVE**2))
       YM=SY/PN
       XM=SX/PN
       C=YM-S*XM
      RKLS=S
      RKLS=RKLS*VFAC
  715 GO TO (128,29,29),IORD
  128 PCENT=CONC(N)/AO*100.
      GO TO 103
   29 PCENT=CONC(N)/BO*100.
  103 IF(SENSE SWITCH 2 )118,119
  119 PRINT 27
   27 FORMAT(7X13HCONCENTRATION12X4HTIME15X14HRATE CONSTANT    )
      DO 517 I=1,N
  517 PRINT617,CONC(I),TIME(I),RK(I)
  617 FORMAT(8XE11.4,10XF8.2,14XE11.4   )
      PRINT 41
      PRINT 31,RKLS
```

```
   31 FORMAT(12X34HLEAST SQUARES RATE CONSTANT      = E11.4  )
      PRINT 32,AVE
   32 FORMAT(12X34HAVERAGE RATE CONSTANT            = E11.4 )
      PRINT 33,CORR
   33 FORMAT(12X34HCORRELATION COEFFICIENT          = E11.4  )
      PRINT 34,SD
   34 FORMAT(12X34HSTANDARD DEVIATION FROM MEAN     = E11.4  )
      PRINT 131,BO
  131 FORMAT(12X34HESTER CONCENTRATION              = E11.4   )
      IF(AO)713,712,713
  712 PRINT 133,BO
  133 FORMAT(12X34HCATALYST CONCENTRATION           = F6.4,1HN  )
      GO TO 79
  713 PRINT 133,AO
   79 PRINT 75,PCENT
   75 FORMAT(12X34HPERCENTAGE OF REACTION FOLLOWED = F6.2   )
      PRINT 81
  118 IF(SENSE SWITCH 1 )500,501
  500 PUNCH 81
      PUNCH 200
      PUNCH 41
      PUNCH 27
      DO 117 I=1,N
  117 PUNCH 617,CONC(I),TIME(I),RK(I)
      PUNCH 41
      PUNCH 31,RKLS
      PUNCH 32,AVE
      PUNCH 33,CORR
      PUNCH 34,SD
      PUNCH 131,BO
      IF(AO)1713,1712,1713
 1712 PUNCH 133,BO
      GO TO 1715
 1713 PUNCH 133,AO
 1715 PUNCH 75,PCENT
  501 GO TO 333
      END
```

PAGE 2

```
C       PROGRAM TO CALCULATE DG DH DS
C       LAST CARD CONTAINS A NEGATIVE RATE CONSTANT
C       FIRST DATA CARD CONTAINS IDENTIFICATION
        DIMENSION T(20),RK(20),X(20),Y(20)
        WRITE(3,33)
   33   FORMAT(1H1)
   10   WRITE(3,11)
   11   FORMAT(////)
        READ(2,13)
        WRITE(3,13)
   13   FORMAT(20X,50H
        WRITE(3,14)
   14   FORMAT(/)
        DO18J=1,20
        READ(2,16)T(J),RK(J)
   16   FORMAT(F10.3,E10.4)
        IF(T(J))19,17,17
   17   T(J)=T(J)+273.1
        X(J)=1./T(J)
   18   Y(J)=ALOG(RK(J)/T(J))
   19   N=J-1
        PN=N
        SX=0.
        SY=0.
        SXSQ=0.
        SXY=0.
        SYSQ=0.
        DO21J=1,N
        SX=SX+X(J)
        SY=SY+Y(J)
        SYSQ=SYSQ+Y(J)*Y(J)
        SXY=SXY+X(J)*Y(J)
   21   SXSQ=SXSQ+X(J)*X(J)
        PA=SXSQ-(SX*SX)/PN
        QA=SYSQ-(SY*SY)/PN
        BA=SXY-(SX*SY)/PN
        S=BA/PA
        CORR=SQRT(ABS((BA**2)/(PA*QA)))
        SD=SQRT(ABS((QA-(BA*BA)/PA)/(PN-2.)))
        YM=SY/PN
        XM=SX/PN
        C=YM-S*XM
        DH=-1.9872*S
        WRITE(3,22)
   22   FORMAT(12X,'DEG C.                                    RATE CONSTANT')
        TEMP=25.
   23   TEMP=TEMP+273.1
        Z=S/TEMP+C
        RATE=TEMP*EXP(Z)
        TEMP=TEMP-273.1
        WRITE(3,24)TEMP,RATE
```

```
   24 FORMAT(13X,F4.1,29X,E10.4)
      TEMP=TEMP+10.
      IF(TEMP-65.)23,23,25
   25 TDS=318.1
      Z=S/TDS+C
      RKDS=TDS*EXP(Z)
      DS=-47.216+DH/TDS+1.9872*ALOG(RKDS/TDS)
      DG=DH-TDS*DS
      WRITE(3,14)
      WRITE(3,26)DH
   26 FORMAT(16X,'ENTHALPY CHANGE     ='F10.2)
      WRITE(3,27)DS
   27 FORMAT(16X,'ENTROPY CHANGE      ='F10.2)
      WRITE(3,28)DG
   28 FORMAT(16X,'FREE ENERGY CHANGE ='F10.2)
      WRITE(3,29)CORR
   29 FORMAT(16X,'CORRELATION         ='F8.5)
      WRITE(3,30)C
   30 FORMAT(16X,'INTERCEPT           ='E10.4)
      WRITE(3,31)SD
   31 FORMAT(16X,'STANDARD DEVIATION ='E10.4)
      SDS=SD/SQRT(SXSQ-(SX*SX)/PN)
      WRITE(3,32)SDS
   32 FORMAT(8X,'STANDARD DEVIATION IN SLOPE = 'E11.4)
      GO TO 10
      END
```

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